Intramolecular proton transfer of 2-hydroxy-1-naphthaldehyde semicarbazone and thiosemicarbazone in ground and lowest excited singlet states: A comparative experimental and computational study

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Photophysics of 2-hydroxy-1-naphthaldehyde semicarbazone (2HNS) and the corresponding thiosemicarbazone (2HNT) are explored in n-heptane and methanol as solvents, focusing on the intramolecular proton transfer (IPT) in the ground (S₀) and the first excited singlet (S₁) states using absorption, steady state and time-resolved fluorometric techniques. The feasibility of the IPT process in the two molecular systems has also been compared. Experiments confirm that for both the compounds IPT takes place in the lowest excited singlet state (S₁), but not in the ground state (S₀). Ab-initio quantum chemical calculations provide support to the experimental findings. Simulated potential energy curves (PEC) in the two electronic states imply that the IPT process is endothermic in the S₀ state but becomes exothermic in the S₁ state for both the probes. PECs also reveal that compared to the ground state the activation barrier for the IPT process is reduced appreciably in the S₁ state. The IPT process, thus, becomes feasible both thermodynamically and kinetically in the S₁ state but not in the S₀ state. The experiments and calculations, however, reveal that the excited state intramolecular proton transfer process is relatively more viable for 2HNS compared to 2HNT. Further, the work demonstrates that any of the suitably chosen structural parameters leading to the unique transition state and yielding the same values of the reaction parameters can be taken as the reaction coordinate to follow the progress of the intramolecular prototropic process.

Keywords: Intramolecular proton transfer, Tautomers, Fluorescence, Potential energy curves

Photochemical research has traditionally been a field of enlivening interest to the scientists owing to the profusely modulated photophysics of many of the compounds emerging through photoexcitation. This eventually leads to several interesting photophysical phenomena like excited state inter- and intramolecular proton transfer, charge transfer (CT), energy transfer (ET) etc. Because of its varied applications in scientific and technological arena, study of the excited state intramolecular proton transfer (ESIPT) has been an active area of research since the first explorative observation of the phenomenon during the mid-twentieth century.1,2 ESIPT occurs in molecules containing both acidic and basic groups in close proximity that may rearrange in the excited electronic state via a proton transfer to form the phototautomer.2-3 ESIPT active molecules often show dual emission; one being the normal emission from the local excitation and the other largely red-shifted, corresponding to the tautomer formed in the excited state by the intramolecular proton transfer.2,4 The characteristics of the normal and the tautomer emissions and their relative fluorescence intensities depend very much on the polarity, proticity and the pH of the medium.4-7 The ESIPT phenomenon makes these molecules attractive to design fluorescence sensors, laser dyes, LEDs, UV filters, molecular switches, etc.8-12 ESIPT compounds are also used as fluorescent probes to decipher the biomimicking microenvironments.13-16

The phenomenon of proton transfer in the excited states has been established for a large number of molecular systems through experimental as well as computational works.17-28 Many of such ESIPT studies have been carried out in naphthalenic moieties that serve as chromophores to probe the reaction fluorometrically. In one of our recent works we have established the occurrence of ESIPT process in 2-hydroxy-1-naphthaldehyde semicarbazone (2HNS), a derivative of the well known ESIPT probe 2-hydroxy-1-naphthaldehyde.22 Other examples include esters of o-hydroxy naphthoic acid,23 3-hydroxy-2-naphthaldehyde,24 2-hydroxy-1-naphthaldehyde,25 3-hydroxy-2-naphthoic acid,26 benzothiazoles,27
1-hydroxy-2-naphthyl-s-triazine, etc. All these compounds exhibit the general characteristics of ESIPT systems like dual emission, dependence on solution pH and proticity. In the present article, we have extended the study to 2-hydroxy-1-naphthaldehyde thiosemicarbazone (2HNT), another analogue of 2HNS with the intention to compare the relative feasibility of the ESIPT process in the two molecular systems which are structurally quite similar, differing only in the substituent attached to the C₂₂ centre (vide Scheme 1). Functionally, both the molecular systems serve excellent purposes in synthetic inorganic, organometallic and bioinorganic chemistry since they are specially designed ligands with a favorable conformation for metal ion binding. The various binding modes of these ligands with different metals are of considerable importance; they form metal chelates with platinum, iron, tin, etc., and are also reported to have antitumour activity. The molecules are reported to interact with DNA making them bioactive. Since the specific orientation of the proton donor and acceptor sites of these important compounds seems to be favorable for intramolecular proton transfer (IPT) reaction, we have studied the IPT process in both ground and photoexcited states, an endeavor which is new for these compounds.

In the present article we report comparison of the IPT related spectroscopic observations of 2HNS and 2HNT based on their spectral and photophysical properties. The study is made in two solvents, namely n-heptane and methanol, differing widely in terms of polarity and proticity, both of which play a significant role in the IPT process. Methanol is remarkably more polar than n-heptane (the dielectric constants are 32.6 and 1.92 respectively). Also, the proticity or hydrogen bonding ability of methanol is much more compared to that of n-heptane. In polar and protic solvents the proton transfer sites are bonded to the solvents through intermolecular hydrogen bonding and one hardly observes the tautomer which is supposed to be formed through ESIPT. However in aprotic and apolar solvents (like alkanes) there is no intermolecular hydrogen bonding between the probe and the solvent. On the other hand, an intramolecular hydrogen bonded closed structure predominates that acts as the precursor of the ESIPT process, leading to the formation of the corresponding tautomer.

The impact of these factors can be demonstrated by studying the photophysics of the prototropic probes in an intermediate solvent like acetonitrile (ACN) where one really observes an intermediate situation in terms of IPT process. The fluorescence spectrum of 2HNT
in ACN is presented in Fig. S1 (Supplementary Data) as a representative of the two molecular systems. In n-heptane the photoproduced tautomer dominates while it is hardly formed in methanol (vide supra). In ACN, fluorescence of both the species is evident (Supplementary Data, Fig. S1). Steady state absorption and emission as well as time resolved fluorometric techniques are exploited in the present study. HF/6-31G** and CIS/6-31G** levels of calculations are used to simulate the ground state and the excited state PECs respectively. Consistent with the experimental observations, the simulated potential energy curves reveal that the IPT reaction is feasible, both thermodynamically and kinetically, in the $S_1$ state but not in the ground state for both the compounds. It is however revealed that the IPT reaction is more favorable in 2HNS than in 2HNT. The study also establishes that either of the distances of the transferable hydrogen from the oxygen atom (wherefrom it is dissociated during the IPT reaction) or the nitrogen atom (to which it is attached) can be considered as the reaction coordinate to follow the course of the prototropic process.

**Materials and Methods**

2HNS and 2HNT (Scheme 1) were synthesized as described elsewhere, 29-31 and were purified by recrystallization from ethanol. The solvents, n-heptane and methanol, were of UV spectroscopic grade (Spectrochem, India). Methanol was used as received, while n-heptane was dried by refluxing with sodium. 35 Due to the low solubility of the compounds in n-heptane, their solutions were prepared by sonication followed by filtration.

Absorption and emission spectral measurements were made on Shimadzu UV-2450 absorption spectrophotometer and Spex Fluorolog-2 spectrofluorometer equipped with DM3000F software respectively. Fluorescence lifetimes were determined from the time resolved fluorescence decays by the method of time-correlated single-photon counting (TCSPC). Nano-LED excitation source at 370 nm and TBX-04 detector (both IBH, UK) were used resulting in the instrument response time ~1 ns for the set-up. IBH DAS-6 decay analysis software was exploited for the analysis of the fluorescence decays. Goodness of fit was assessed from the $\chi^2$ criteria and visual inspection of the randomness of the residuals of the fitted function to the data. Throughout the study the sample concentrations were kept in the range of $10^5$–$10^6$ mol dm$^{-3}$ to avoid aggregation and inner filter effect due to re-absorption. All the experiments are performed with air equilibrated solutions at room temperature (300 K).

**Computational procedure**

Considering the bulk of calculations required for the two relatively large molecular systems, we have adopted the Hartree-Fock (HF) level of calculation for the present work, although density functional theory (DFT) has established its superiority in explaining the proton transfer reactions. 5,20-24,36 The calculations were performed with Gaussian 03 suite of the quantum chemical programs. 37 The ground state geometry of 2HNS and 2HNT were fully optimized using HF at 6-31G** level. The calculations provided the energies of the molecular systems in the ground state. The potential energy curves (PEC) for the ground state intramolecular proton transfer process (GSIPT) were then constructed using the energies ($E_g$) at the optimized geometries at different pre-fixed O-H distances over a wide range (0.8–2.3 Å) for both 2HNS and 2HNT.

The excitation energies were calculated from the vertical transitions of the optimized ground states at pre-fixed O-H distances at the CIS level. The presenting transition energies ($\Delta E_{g\rightarrow j}$), correspond to the excitation of an electron from the HOMO orbital ($\phi_i$) to the LUMO orbital ($\phi_j$). The energy of the excited state ($E_j$) was calculated as $E_j = E_g + \Delta E_{g\rightarrow j}$. The PEC for the ES1PT process is then simulated using $E_j$. 17,19,20,22,25,36,39,40 Interaction site model using the self-consistent field method was followed for the computational approach to study the IPT reaction. 22,41

**Results and Discussion**

**Absorption studies**

The absorption spectra of 2HNS and 2HNT in n-heptane (non-protic and non-polar) and methanol (protic and polar) are shown in Fig. 1. In both the solvents, the probes exhibit structured absorption spectra. Broadly, there are two bands, one covering the range 300–335 nm and the other within 335–420 nm for both the systems. Both the bands reveal structural patterns. Although the peak positions do not differ appreciably in the two solvents, there are differences in the band patterns. This is attributed to the presence of two different absorbing species in the two solvents. Consistent with the existing literature on similar systems, one may be assigned to the
intramolecularly hydrogen bonded closed conformer\textsuperscript{2} (in \textit{n}-heptane) while the other to the open enolic conformer, intermolecularly hydrogen bonded to methanol.\textsuperscript{2} Absence of any new absorption spectral band in methanol rules out the occurrence of intermolecular proton transfer in the ground state. The low acid dissociation constant of the skeletal molecular system, 2-naphthol, with a similar –OH group in the ground state (\(pK_a = 9.49\)) justifies the non-occurrence of the IPT process in the ground state of both the systems.\textsuperscript{22,42} A lower \(pK_a^*\) (2.75) value of 2-naphthol in the excited state (\(S_1\)) however suggests that in the photoexcited state the –OH proton may be dissociated from the molecule rather easily.\textsuperscript{42}

**Steady state emission studies**

Figure 2 depicts the emission spectra of 2HNS and 2HNT in \textit{n}-heptane and methanol. Upon photoexcitation (\(\lambda_{\text{exc}} = 330\) nm), both the probes yield structured emissions. In methanol, the two molecular systems yield emission bands peaking at ~440 nm and ~425 nm respectively, ascribed to the normal emissions from the corresponding enolic species. For both the systems, in the non-polar solvent \textit{n}-heptane, however, in addition to the normal bands, prominent and largely red-shifted structured emissions appear peaking at ~496 nm (shoulder at ~525 nm) and ~510 nm (shoulder at ~545 nm) for 2HNS and 2HNT respectively. The low energy intense emissions are found to be sensitive to the protic character of the solvent. Thus, these emissions appear characteristic for the tautomeric species of the probes produced in the photoexcited state.\textsuperscript{20-27,38-40,43,44} Insignificant intensity of the tautomer fluorescence in methanol solution implies that stabilization of the normal forms through intermolecular hydrogen bonding with the protic solvent inhibits the ESIPT process. For each of the two probes, the relative intensities of the normal to the tautomer emissions remain invariant with a change in the concentration of the compounds in the range of concentration studied (~10\textsuperscript{-5}–10\textsuperscript{-6} mol dm\textsuperscript{-3}), corroborating the intramolecular character of the proton transfer process.

The overlays of the absorption and emission spectra of 2HNS and 2HNT in \textit{n}-heptane and methanol solvents are shown in Fig. 3. From the intersections of the normalized fluorescence and fluorescence excitation spectra, the zero-zero transitions of the two molecular systems were determined in the two solvents. For 2HNS these are seen at 391 nm and 390 nm in \textit{n}-heptane and methanol respectively, while the same for 2HNT appear at 393 nm and 392 nm in the respective solvents.

**Fluorescence lifetimes of the prototropic species**

The fluorescence decays of 2HNS and 2HNT at room temperature were monitored in \textit{n}-heptane and methanol. We were unable to see any growth for the tautomer emission for either of the probes, indicating that the ESIPT process is too fast to be monitored with our set-up with an instrument response time of ~1 ns. This is consistent with the ESIPT systems in general, where the transferable proton is in a favored geometry through intramolecular hydrogen bonding prior to the proton transfer.\textsuperscript{2,22} Since the response of our set-up is too slow to resolve the kinetics of the ESIPT process, details of the time-resolved analysis of the decays have been omitted and only fluorescence lifetimes of the normal and the tautomer species of the two probes at their respective emission bands have been reported. For 2HNS, the monitoring wavelengths are 440 nm and 540 nm while for 2HNT these are 425 nm and 530 nm for the normal and the tautomer species respectively. In \textit{n}-heptane the fluorescence lifetimes of the normal forms of 2HNS and 2HNT are determined to be 0.08 ns and 0.3 ns respectively, and for the tautomers of the corresponding compounds as 0.3 ns and 1.22 ns respectively. The
Quantum chemical calculations

The ground state optimized geometries of 2HNS and 2HNT were obtained using HF/6-31G** level of calculation. Since crystal data of neither 2HNS nor 2HNT are available in the literature, to check the reliability of our calculations we have applied the same method of calculation to optimize the geometry of another analogous molecular system, namely, 2-hydroxy-1-naphthaldehyde methyl thiosemicarbazone (2HNMT) (Supplementary Data, Scheme S1) whose crystal structures is reported in the literature. The calculated ground state optimized geometric parameters 2HNMT and the corresponding literature data are given in Table S1 (Supplementary Data). The correspondence between the calculated parameters and the crystallographic data establishes the reliability and acceptability of our method of quantum chemical calculations. The same method of calculation was then applied to optimize the ground state geometries of 2HNS and 2HNT and the calculated geometric parameters are tabulated in Table 1 for the two molecular systems.

Potential energy curves (PECs) in the ground ($S_0$) and the lowest excited singlet states ($S_1$) were

Fig. 3—Absorption (black) and emission (red) spectral overlay of 2HNS in (a) n-heptane and (b) methanol and of 2HNT in (c) n-heptane and (d) methanol. The spectra are normalized at the low energy absorption band and the normal emission band. [Inset in (a) and (c) shows the amplified absorption (black) and emission (red) spectral overlay. $\lambda_{exc} = 330$ nm].

Fig. 4—Decay profiles of (a) 2HNS and (b) 2HNT in n-heptane. [The black profiles show the instrument response functions (IRF). $\lambda_{exc} = 370$ nm].

gross decay profiles of both the compounds are presented in Fig. 4.
constructed to envisage the intramolecular proton transfer of 2HNS and 2HNT in these two electronic states. For both the molecular systems we have considered the distances of the transferable hydrogen (H\textsubscript{18}) from the oxygen atom (O\textsubscript{17}, wherefrom it is dissociated during the IPT reaction) as well as from the nitrogen atom (N\textsubscript{20}, to which it gets attached to) as the independent reaction coordinates following the “distinguished coordinate” approach as proposed by Sobolewski and Domcke.\textsuperscript{45,20,22,24} The PECs were constructed considering the probes in vacuum and are depicted in Fig. S2 (Supplementary Data). Potential energy surfaces for the intramolecular proton transfer reaction of both the compounds were also simulated in the S\textsubscript{0} and S\textsubscript{1} states taking, simultaneously, O\textsubscript{17}-H\textsubscript{18} distance and O\textsubscript{17}····H\textsubscript{18}····N\textsubscript{20} angle as the reaction coordinates (Fig. 5). In both the electronic states the simulation reveals double well potentials, one corresponding to the normal and the other to the tautomer. The PECs reveal that in the ground state the global minimum rests on the normal form of the probes while the same corresponds to the tautomer form in the S\textsubscript{1} state. This suggests that in the ground state the most stable species is the normal form, whereas in the photoexcited state it is the tautomer that prevails justifying the occurrence of ESIPT for both the molecular systems.

Calculations suggest that in the ground state, the normal form of 2HNS is more stable than the tautomer by 2.83 kcal/mol ($\Delta H = +2.83 \text{ kcal/mol}$ for the formation of the tautomer through IPT) and the same in the case of 2HNT is 3.67 kcal/mol ($\Delta H = +3.67 \text{ kcal/mol}$). In the S\textsubscript{1} state, however, the corresponding tautomers are found to be more stable for both the systems ($\Delta H = -3.78 \text{ kcal/mol}$ and $-0.7 \text{ kcal/mol}$ for the two compounds respectively). Thus, the intramolecular proton transfer reaction of both 2HNS and 2HNT appears to be thermodynamically unfavorable in the ground state as the process leads to endothermicity. On the other

<table>
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<th>Molecular Parameters</th>
<th>Calc. Data</th>
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<tr>
<td></td>
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*Structures of 2HNS and 2HNT are given in Scheme 1.*
hand, in the photoexcited state the process leads to exothermicity and hence seems viable. This is consistent with the experimental findings where the much red-shifted tautomer emissions are observed for both the systems in \( n \)-heptane medium. The PECs also qualitatively point towards the feasibility of the IPT reaction from the kinetic point of view. Calculations reveal that the activation energies \( (E_{\text{act}}) \) for the intramolecular proton transfer process of both the probes are reduced appreciably in the photoexcited states \( (S_1) \) compared to those in the corresponding ground states \( (S_0) \), favoring the prototropic transformation in the \( S_1 \) state relative to the \( S_0 \) state. The calculated \( E_{\text{act}} \) values are 14.23 kcal/mol and 8.60 kcal/mol in the \( S_0 \) and \( S_1 \) states of 2HNS respectively. The same for 2HNT are calculated to be 13.63 kcal/mol and 9.19 kcal/mol in the two states. Although reduced to a large extent from the ground state values, the activation energies still appear to be too high to make the ESIPT process instantaneous. This can be argued from two angles: either the level of calculation is not high enough to give the quantitative estimate of the activation energies or the molecules acquire the required activation energies in the photoexcited state from the photon energy. Thus, although both the thermodynamic \( (\Delta H) \) and kinetic \( (E_{\text{act}}) \) factors go against the IPT process in the ground state, the ESIPT process is favored for both the molecular systems. The calculated thermodynamic and kinetic parameters of the two probes in the \( S_0 \) and \( S_1 \) states are collected in Table 2. The numeric values of \( \Delta H \) and \( E_{\text{act}} \) suggest that the ESIPT process is relatively more viable in 2HNS compared to 2HNT. This is evidenced by the experimental observation where a higher relative intensity of the tautomer to the normal fluorescence is observed for 2HNS as compared to that for 2HNT (vide fluorescence spectra in \( n \)-heptane in Fig. 2). The difference in the feasibility of the ESIPT process for the two probes is rationalized from the structural aspect of the molecules. The geometries of 2HNS and 2HNT are quite similar apart from the difference in the substitution at the C\( _{22} \) centre being O for 2HNS and S for 2HNT. Because of the bulkier size of the sulfur atom as compared to the oxygen atom, the steric factor at the C\( _{22} \) centre is greater for 2HNT than for 2HNS. The bulky S atom possibly imposes a restriction on the transfer of the H\( _{18} \) atom from O\( _{17} \) to N\( _{20} \) centre in the case of 2HNT whereas the same restriction in the case of 2HNS is much less. Thus, the steric factor is ascribed to play a role in imposing a restriction on the proton transfer process in 2HNT over that in 2HNS, making the latter more viable towards ESIPT.

It is pertinent to mention here that the calculations were done considering the molecular systems in vacuum and solvation effect was not taken into account. Limitations in computation facility for such calculations restricted us from performing these calculations. Since ESIPT takes place preferably in apolar aprotic solvents the relevant data are not expected to be disturbed very much since the solvation effects should be less in these solvents. However, in solvents like methanol inclusion of the solvation is likely to disturb the calculated data appreciably. Looking at the ESIPT aspect where experimental observations reveal that the ESIPT is restricted severely in methanol, the relevance of the solvation effect is reduced in this particular context.

The HOMO-LUMO pictures of the normal form, transition state and tautomeric forms of 2HNS and 2HNT are depicted in Fig. 6. For both the molecular systems the electron density pictures reveal that the electron density on O\( _{17} \) is reduced appreciably from HOMO to LUMO upon photoexcitation, and thus, offer a justification for the occurrence of the IPT process in the excited state and not in the ground state.

To see if more than one independent parameter can be considered as reaction coordinate for scanning the progress of the IPT reaction, we have chosen O\( _{17} \)─H\( _{18} \) and H\( _{18} \)─N\( _{20} \) distances since these two geometrical parameters are primarily associated with the

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### Table 2—\( \Delta H \) and \( E_{\text{act}} \) for the IPT process of 2HNS and 2HNT in \( S_0 \) and \( S_1 \) states

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<th>Electronic state</th>
<th>2HNS</th>
<th>2HNT</th>
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<tr>
<td></td>
<td>Heat of reaction ( (\Delta H) ) (kcal/mol)</td>
<td>Activation energy ( (E_{\text{act}}) ) (kcal/mol)</td>
</tr>
<tr>
<td>( S_0 )</td>
<td>+ 2.83</td>
<td>14.23</td>
</tr>
<tr>
<td>( S_1 )</td>
<td>- 3.78</td>
<td>8.60</td>
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</table>
intramolecular proton transfer process. Our intention was to see if the choice of either of the reaction coordinates leads to the same unique transition state (TS). With this objective the potential energy curves were computed to follow the progress of the IPT process taking the two parameters as the independent reaction coordinates. At each point of calculation the angle $\text{O}_17 \cdots \text{H}_18 \cdots \text{N}_20$ was determined from the optimized geometries with the pre-set values of the parameter serving as the reaction coordinate.
Figure 7 representing the variation of this angle with a change in either of the reaction coordinates for both 2HNS and 2HNT indicates unique transition states for 2HNS and 2HNT with $O_{17}\cdots H_{18}\cdots N_{20}$ angle at 149.42° and 148.94° respectively. Characteristic values of $O_{17}\cdots H_{18}$ and $H_{18}\cdots N_{20}$ distances are obtained at the corresponding transition states. Attainment of the same transition state from either parameter as reaction coordinate confirms the uniqueness of the TS and establishes that either of $O_{17}\cdots H_{18}$ or $H_{18}\cdots N_{20}$ may be chosen as the reaction coordinate to monitor the progress of the prototropic process.

Conclusions

A comprehensive and comparative picture of the intramolecular proton transfer reaction of two compounds potentially important in synthetic inorganic chemistry as well as biochemistry, namely, 2-hydroxy-1-naphthaldehyde semicarbazone (2HNS) and the corresponding thiosemicarbazone (2HNT) in the ground ($S_0$) and the lowest excited singlet ($S_1$) states is presented. Results reveal that for both 2HNS and 2HNT, the IPT process is restricted in the ground state, but takes place in the photoexcited state.

Ab initio based quantum chemical calculations at HF/6-31G** level imply that the prototropic reaction is endothermic in the ground state while in the $S_1$ state it becomes exothermic for both the probes. Activation energies are also found to decrease appreciably in the $S_1$ state compared to those in the corresponding $S_0$ state. Thus, both the thermodynamic and the kinetic factors favor the IPT process to occur in the photoexcited state. A relatively less favorable situation for 2HNT as compared to 2HNS to undergo the ESIPT reaction is ascribed to a greater steric effect exerted by the bulkier sulfur atom in the former. The study further demonstrates that either of $O_{17}\cdots H_{18}$ or $H_{18}\cdots N_{20}$ distances may be chosen as the reaction coordinate to follow the progress of the ESIPT process since both approach give the same transition state along with the same reaction parameters.

Supplementary Data

Supplementary data associated with this article, viz., Figs S1 and S2, Scheme S1 and Table S1 are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_53A(01)17-26_SupplData.pdf.

Acknowledgement

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