A fluorescence emission study of nitro- and nitromethyl-substituted 1,4-diarylbutadienes in solid state

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Received 26 March 2001; accepted 4 July 2001

1-(4-Nitrophenyl)-4-phenylbuta-1E,3E-diene 1, 1,4-di-(4-nitrophenyl)buta-1E,3E-diene 2, 1-phenyl-2-methyl-4-(4-nitrophenyl) buta-1E,3E-diene 3, and 1,4-di-(4-nitrophenyl)2-methylbuta-1E,3E-diene 4 have been synthesized and their fluorescence emissions in solid state in comparison with their ambient temperature fluorescence emissions in organic solvents of varying relative permittivity and in ethanol-methanol matrix at 77 K have been investigated. It has been found that while the UV-vis absorption of the dienes in solution phase largely remains unaffected by solvent polarity, the fluorescence maximum (λfl max) gets significantly altered and a much red-shifted λfl max is observed in solvents of relatively higher relative permittivity (e.g., polar solvents like acetonitrile and methanol). In ethanol-methanol glass at 77 K, the fluorescence of the dienes gets significantly blue-shifted. In solid state also a red-shifted fluorescence is observed, but the red-shift is not as pronounced as in polar solvents. However, it is significantly red-shifted as compared to in solvents having relatively lower relative permittivity (e.g., the non-polar solvents like 1,4-dioxane and THF). The fluorescence spectra of nitro-diienes, particularly 2 and 4 in solid state are significantly red-shifted as compared to their fluorescence emission in relatively non-polar solvents. Further, for the mono-nitro substituted dienes 1 and 3, the solid state fluorescence emission is similar to that observed in relatively non-polar solvents. The results have been discussed in terms of the singlet excited states of the dienes having different polarity and geometry. It has been suggested that in solution phase in addition to the fluorescence emission from the initially prepared planar locally excited state, the fluorescence emission in these dienes can occur from intramolecular charge transfer excited state and in some cases even from a non-planar, dipolar conformationally relaxed intramolecular charge transfer excited state. The red-shifted emission of these dienes in solid state when compared to that in relatively less polar solvents, and in another highly condensed media such as ethanol-methanol glass at 77 K indicates that the solid state fluorescence of the dienes does not originate from conformationally relaxed excited states. The solid state fluorescence emission of the dienes has been attributed to excimer and intramolecular charge transfer excited state with planar geometry. Further, the role of energy level re-ordering of the two lowest excited states of the dienes, influencing the fluorescence properties has also been discussed.

Excited state charge transfer phenomenon is important in several biological and chemical systems and in this context a great deal of attention has been focused on the excited state properties of organic chromophores. Donor-acceptor diphenylpolyenes present interesting system for excited state charge transfer studies and recently we have reported solvatochromic fluorescence emission from donor-acceptor 1,2-diylylethenes and 1,4-diphenylbutadienes in solution phase. Particularly, the nitro-substituted 1,4-diphenylbutadienes have been found to exhibit highly solvatochromic fluorescence, in contrast to diphenylbutadienes substituted with groups such as cyano. Such fluorescence properties of these donor-acceptor dienes have enabled them to function as fluorescence probes for the microenvironment of organized assemblies. The solvatochromic fluorescence behaviour of the donor-acceptor compounds have been discussed in terms of the involvement of conformationally relaxed intramolecular charge transfer excited states. Additionally, the solvent and substituent induced state reversals of the two lowest excited states (viz, A* and B* excited states) of these chromophores have also been considered to be of consequence in the photo-processes of these compounds. In view of this, it was of much interest to examine the emission behaviour of donor-acceptor diphenylbutadienes, particularly nitrodienes, in the solid state.

The excited state properties of diphenylpolyenes have extensively been investigated and several
excellent reviews of the subject are available\textsuperscript{9-16}. Some photochemical and photophysical studies of aroylalkenes and related compounds in solid state have also been reported and excellent account of these are also available\textsuperscript{17-23}. In general, the spectroscopic and photochemical properties of these compounds in the solid state are controlled by their crystal structure and topological factors. The photodimerization of aroylalkenes in solid state is known and it is believed to occur via the intermediacy of excimeric species. 

1,4-Diphenylbutadienes substituted with chloride group are known to show emission from the excimer state and also give cyclodimerization product\textsuperscript{24-26}. Recently, we have reported fluorescence and photodimerization of 1,4-diphenylbutadienes having cyano substituent on C=C double bond in the diene moiety and discussed the photochemical and photophysical results in terms of the involvement of excimer and ground state molecular aggregates\textsuperscript{27}.

Thus, the solution state photophysical and photochemical studies of diphenylpolyenes are widely reported while similar studies in solid state have received little attention. The absence of a systematic fluorescence study of donor-acceptor diphenylbutadienes in solid state together with the interesting solvatochromism observed in nitro-diphenylbutadienes prompted us to undertake this study. Thus, herein we report a fluorescence study of nitro-substituted 1,4-diphenylbutadienes 1-4 (Figure 1) in the solid state. In this work, dienes 1-(4-nitrophenoxy)-3-phenylbuta-1E, 3E-diene 1, 1,4-di(4-nitrophenyl)buta-1E,3E-diene 2, 1-phenyl-2-methyl-4-(4-nitrophenoxy)buta-1E, 3E-diene 3, and 1,4-di (4-nitrophenyl)-2-methylbuta-1E, 3E-diene 4 have been synthesized and a comparative study of the fluorescence emissions of these dienes in the solid state and in organic solvents of varying relative permittivity at ambient temperature and in ethanol-methanol matrix at 77 K has been done. It has been found that in solution phase in addition to the fluorescence emission from initially prepared planar locally excited state, the fluorescence emission in these dienes can occur from intramolecular charge transfer excited state and in some cases even from a non-planar, dipolar conformationally relaxed intramolecular charge transfer excited state. The redshifted emission of these dienes in solid state as compared to in solvents of low relative permittivity (i.e, relatively less polar solvents) and in another highly condensed media such as ethanol-methanol glass at 77 K has indicated that the solid state fluorescence of these dienes does not come from the conformationally relaxed excited states. The solid state fluorescence emission of the dienes has been attributed to excimer and intramolecular charge transfer excited state with planar geometry. Further, the role of energy level re-ordering of the two lowest excited states of the dienes, influencing the fluorescence properties has also been discussed.

\textbf{Results and Discussion}

The UV-vis absorption and fluorescence spectral data for dienes 1-4 are summarized in Tables I and II. The absorption spectra of dienes 1-4 remain largely unaffected by the relative permittivity of the solvent. However, as compared to the solution phase
Table I—UV-vis absorption data of DPB and substituted dienes 1-4 in organic solvents and solid statea

<table>
<thead>
<tr>
<th>Media</th>
<th>Diene λ_{abs max} /nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DPB 1 2 3 4</td>
</tr>
<tr>
<td>1,4-Dioxane</td>
<td>335 375 383 367 372</td>
</tr>
<tr>
<td>THF</td>
<td>335 375 385 367 373</td>
</tr>
<tr>
<td>DMF</td>
<td>335 383 385 378 382</td>
</tr>
<tr>
<td>MeCN</td>
<td>335 378 385 364 375</td>
</tr>
<tr>
<td>MeOH</td>
<td>335 379 385 367 377</td>
</tr>
<tr>
<td>Solid stateb</td>
<td>346, 367 346, 367</td>
</tr>
</tbody>
</table>

a: The absorption spectra are broad ranging in 370 - 500 nm. The λ values indicated are approximately at the highest absorbance. b: In KBr pellet. DPB: 1,4-Diphenylbuta-1,3-diene.

Table II—Fluorescence emission data of dienes in organic solvents, solid statea and at 77 Kb

<table>
<thead>
<tr>
<th>Media</th>
<th>Diene λ_{em max} /nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DPB 1 2 3 4</td>
</tr>
<tr>
<td>1,4-Dioxane</td>
<td>375 495 465 500 483</td>
</tr>
<tr>
<td>THF</td>
<td>375 508 474 517 488</td>
</tr>
<tr>
<td>DMF</td>
<td>375 576 530 576 544</td>
</tr>
<tr>
<td>AcCN</td>
<td>378 606 569 608 583</td>
</tr>
<tr>
<td>MeOH</td>
<td>378 606 569 608 583</td>
</tr>
<tr>
<td>Solid statea</td>
<td>415, 427, 455 480, 510, 517, 499, 529</td>
</tr>
<tr>
<td>77 Kb</td>
<td>379 492 480 488 483</td>
</tr>
</tbody>
</table>

a: In KBr pellet. b: 1:1 (v/v) ethanol-methanol matrix. DPB: 1,4-Diphenylbuta-1,3-diene.

The absorption maximum (λ_{abs max}) observed for the parent unsubstituent diene viz. 1,4-diphenylbuta-1,3E-diene (DPB), the substituted dienes 1-4 exhibit a red-shifted absorption λ_{abs max}. DPB in solution is known to exhibit λ_{abs max} in the region of 330 nm with vibrational structures in 315 and 350 nm regions.4,31 This red shift in λ_{abs max} can be attributed to the mesomeric effect of the substituents. The maximum red shift of about 50 nm is caused in diene 2 having two nitro groups at the para position of the phenyl rings. The presence of a methyl group at the chain C=C double bond as in diene 3 causes lesser red shift, which may be due to steric effects of the methyl group on the conjugative properties of the diene. Similar red-shifted absorption for the nitro-dienes is observed in the solid state. As compared to solution state absorption, the absorptions of substituted dienes in solid state are expectedly much broader and red-shifted by about 60 – 80 nm (Figure 2). In general, the absorption spectra of the nitro-dienes in solid state are characterized by broad bands with wavelength of absorption extending from 370 nm to almost 500 nm. In contrast, the parent unsubstituted diene DPB shows a red shift of only about ~11-32 nm in the solid state as compared to in solution phase. The steric effect of methyl group seen on solution phase absorption spectrum of the dienes is also observed in the absorption spectrum in the solid state. The shift in the solid state absorption of nitro-substituted dienes as compared to parent diene DPB, can be attributed to different crystal arrangement of the substituted diene molecules. Thus, the red-shifted absorption observed in the solid state as compared to the solution media can be due to the formation of J type of aggregates wherein the molecules can be arranged in head-to-tail fashion. Such aggregates exhibiting red-shifted absorption are known to exist in solid thin films of many organics including alkenes, azobenzenes and merocyanine dyes.32

In contrast to a largely insensitive nature of the UV-vis absorption of the nitro-dienes 1-4 towards
solvent polarity, the fluorescence spectra of these dienes are greatly influenced by the solvent polarity. Thus, the fluorescence spectrum of these dienes is characterized by much red-shifted fluorescence maximum ($\lambda_f$ max) when the relative permittivity of the solvent is increased. For instance, the $\lambda_f$ max of diene 3 in polar methanol gets red-shifted by 108 nm as compared to in relatively less polar 1,4-dioxane solution (Table II, Figure 3). The red-shifted fluorescence emission is also observed in the solid state at ambient temperature (Table II, Figure 4).

However, the red shift in solid state fluorescence is less pronounced as compared to in polar solvents. The maximum red shift in $\lambda_f$ max is observed in protic methanol. Thus, in solid state, the dienes exhibit relatively blue-shifted fluorescence emission as compared to the fluorescence emission in methanol solution. The magnitude of red shift in $\lambda_f$ max of mononitro-substituted dienes 1 and 3 is similar. The dinitro-substituted dienes 2 and 4, on the other hand show similar shift in $\lambda_f$ max but of a smaller magnitude as compared to the $\lambda_f$ max shifts in dienes 1 and 3. Thus, while for mononitro-substituted dienes 1 and 3 the shift in solid state fluorescence as compared to in methanol is about 126/96 and 109 nm respectively, for the dinitro-substituted dienes 2 and 4 it is in the range of 52 to 54 nm. Among the four dienes, trisubstituted diene 4 with two nitro groups in the phenyl rings and a methyl group on C=C double bond in the chain exhibits the maximum red shift in the solid state fluorescence. Thus, the solid state fluorescence emission of these dienes is red-shifted as compared to the fluorescence emission in relatively less polar solvents and blue-shifted in comparison to the fluorescence emission in protic-polar methanol or in aprotic-polar acetonitrile and DMF.
At 77 K, these dienes exhibit a significantly blue-shifted fluorescence spectrum (Figure 5), much like what is observed in the relatively non-polar 1,4-dioxane or THF media (Table II). However, the fluorescence spectra in rigid media at 77 K are characterized by fine structures as against relatively broad bands observed in solution phase at ambient temperature. The fluorescence bands at 77 K, however, are less broad than the fluorescence bands for the same diene in the solid state. Further, as compared to in rigid matrix of ethanol-methanol glass at 77 K, the dienes in the solid state fluoresce at longer wavelengths. Additionally, the fluorescence emission spectra of the nitro dienes in solid state are slightly structured. The appearance of vibrational structures in the fluorescence spectra of the dienes in condensed phases indicate minimal effects of the excited state relaxations in the dienes.

Recently, we have demonstrated that fluorescence in donor-acceptor diphenylbutadienes can occur from initially prepared planar locally excited state, planar intramolecular charge transfer (ICT) excited state, and conformationally relaxed, non-planar intramolecular charge transfer excited state. The conformational relaxation in the excited diene can occur by twisting across certain single bond in the molecule and such twisted excited states are highly polar in nature, thereby getting stabilized in polar solvents giving highly red-shifted fluorescence. The fluorescence spectra of dienes 1-4 in solution phase, particularly in solvents having high relative permittivity can also be attributed to conformationally relaxed intramolecular charge transfer excited state having non-planar geometry and dipolar character. Owing to different electronegativities present in the substituted dienes, intramolecular charge transfer in the diene excited state can occur via twisting of the bond between the nitro group attached to the phenyl ring. A possible twisting of the C-C single bond of the dienyl moiety is highly improbable, as it will require a relatively larger volume of activation. Furthermore, large
amplitude motion such as the beginning of cis-trans 
soomerization is also highly unlikely as time required 
for such motion would be too great to occur within a 
fluorescence lifetime. Photochemical studies of the 
nitro-dienes in solution have shown that the dienes e. g. 1 and 2) do not show formation of cis isomer 
when irradiated in organic solvents. It is possible 
that the absorbed photon energy is dissipated by 
wisting of single bond connecting the nitro group 
with the aromatic ring. That the single bond twisting 
occurs in these dienes is supported by the blue-shifted 
fluorescence emission observed for the dienes in 
ethanol-methanol matrix at 77 K. Under the rigid 
condition of ethanol-methanol glass, conformational 
relaxation via single bond twist is highly improbable. 
Therefore, formation of dipolar twisted excited states 
in the rigid media is inhibited and the fluorescence 
emission originates from the planar locally excited 
state.

The fluorescence properties of the dienes in solution 
are also expected to be influenced by the 
relative energy level ordering of the two singlet 
excited states viz. \( \text{A}_g^* \) and \( \text{B}_u^* \), which are likely to be 
separated only by a low energy barrier. It is believed 
that the \( \text{B}_u^* \) state is ionic in nature while the 
\( \text{A}_g^* \) has a covalent character. In polar solvent, the \( \text{B}_u^* \) 
is expected to be stabilized. Thus, the red shift in the 
fluorescence emissions of these dienes can be due to 
preferential stabilization of the \( \text{B}_u^* \) state. In non-polar 
solvent, the \( \text{A}_g^* \) state may be the lowest excited state 
giving the fluorescence emission.

The position of the fluorescence emission of the 
nitro-dienes in solid state indicates that the change in 
their nuclear configuration during the interval 
between absorption and re-emission is small. In order 
for fluorescence emission to occur at much longer 
wavelength major re-organization must begin during 
the motions of the molecules within the crystal 
structure. Since such a movement is not possible in 
highly condensed media, wherein molecules are 
tightly bound and experience high local restrictions 
such as in solids, the dienes should fluoresce at lesser 
wavelengths. However, the fluorescence spectra of 
nitro-dienes in solid state, particularly 2 and 4 are 
significantly red-shifted as compared to their

fluorescence emission in solvents having relatively 
lesser relative permittivity (e.g., 1,4-dioxane and 
THF, Table II). The red-shifted fluorescence 
emissions of these dienes in solid state as compared to 
in relatively less polar solvents, and in another highly 
condensed media such as ethanol-methanol glass at 77 
K indicate that the solid state fluorescence emission of 
these dienes may be due to the interaction that occurs 
in the excited state leading to a new species, probably 
an excimer. The blue-shifted emission of the dienes in 
solid state as compared to in relatively polar methanol 
strongly suggests absence of any significant 
conformational relaxation leading to twisted structure 
of the fluorescent excited state in the solid phase. 
Earlier studies of substituted butadienes (e.g. 1-cyano 
substituted 1,4-diphenyl butadiene and 1-(2,6-di-
chlorophenyl)-4-phenylbuta-1E, 3E-diene) have 
shown that the excimer emission is usually associated 
with a dimer formation in their photoreaction. 
Since a dimer cannot be formed in a fluorescence time 
scale, the red shift in the fluorescence emission with 
respect to the parent diphenylbutadiene DPB is 
attributed to the formation of an excimer species. For 
mononitro-substituted dienes 1 and 3 the solid state 
fluorescence emissions are similar to those observed 
for these dienes in less polar solvents like 1,4-dioxane 
and THF. The fluorescence of mono-nitro substituted 
dienes in solid state, therefore, has origin in a planar 
excited state – either the LE state or the ICT state. 
The involvement of an ICT excited state in the 
fluorescence emissions of dienes 2 and 4 in solid state 
also cannot be ruled out. The fluorescence emissions 
of dienes 2 and 4 in solid state are red-shifted by 52 
and 46 nm respectively with respect to their 
fluorescence emission in relatively less polar 1,4-
dioxane. Such red-shift in \( \lambda_v \) max can occur if the 
excited state undergoes intramolecular charge 
separation. The ICT state thus formed is lower in 
energy than the planar locally excited state, and hence 
can give fluorescence emission at wavelength longer 
than that is observed from the locally excited state. 
Thus, the solid state fluorescence emissions from the 
nitrodienes can come either from planar ICT states or 
from excimer species. It may be noted here that the 
 solvent-induced re-ordering of the energy levels of the
lowest singlet excited states of the dienes seem to be absent in the solid state.

In conclusion it can be said that the fluorescence missions in nitro-substituted 1,4-diphenylbutadienes in solid state can originate from the planar intramolecular charge transfer excited state or from the excimer species. The conformationally relaxed intramolecular charge transfer excited states are not involved in the solid state fluorescence process of these nitrodienes. However, in solution phase, the fluorescence emissions of these dienes are greatly affected by solvent polarity and non-planar, dipolar intramolecular charge transfer excited states can also be involved in the fluorescence process. The present study has brought out interesting features of the singlet excited state structure and dynamics of donor-acceptor diphenylbutadienes in solution and solid state. It would, however, be interesting to investigate the photochemical behaviour of the nitrodienes in the solid state, as a discussion of the nature of excited states and the corresponding photoprocesses will not be complete without such studies.

Experimental Section

General procedures

Melting points were determined on Veego melting point apparatus using capillary method and are uncorrected. IR spectra were recorded on Impact 400 Nicolet FTIR spectrophotometer in KBr pellets. 1H NMR spectra in CDCl3 as solvent and TMS as internal standard were recorded on a 300 MHz FT NMR instrument available at the Regional Sophisticated Instrument Centre, IIT Bombay. UV-vis measurements were made on Shimadzu UV-260 spectrophotometer. The UV-vis absorption spectra of the dienes in solid state were recorded by taking the solid diene in KBr pellets, which were prepared as per KBr pellet preparation method (for IR studies) in which a small amount of the diene is mixed with KBr and the mixture is compressed to obtain the desired thin KBr pellet. The KBr discs thus prepared was kept in the path of the beam in the spectrophotometer and the spectra were recorded after making necessary corrections for the KBr as baseline. The fluorescence measurements were made on DM1B Spex-fluorolog spectrofluorimeter equipped with accessories for low-temperature emission and solid state studies. The fluorescence spectra were recorded by fixing the excitation monochromator at the absorption maximum (λ\text{ab}\text{max}). The fluorescence spectra in solid state were measured in KBr-sample pellet (prepared by compression method) using front face illumination (22°) by employing accessory 1933F in Spex-fluorolog spectrofluorimeter. The slit widths used are 1 mm for excitation monochromator and 1.5 mm for emission monochromator. The fluorescence measurements at low temperatures were made in ethanol-methanol (1:1 v/v) glass at 77 K. For all the solution phase electronic spectroscopic studies (absorption, fluorescence excitation and emission), 1.0×10^{-5}M solutions of the dienes in respective solvents were used. All the solutions were handled under protective red light conditions. TLC analyses were performed on freshly prepared silica gel G (E. Merck) plates using petroleum ether (60-80°C) and ethyl acetate with suitable polarity as developing solvents. Column chromatography was done on silica gel G (60-120 mesh, E. Merck) using 5-10% ethyl acetate - petroleum ether (v/v) as eluting solvent.

Synthesis of dienes

Dienes 1-4 were synthesized from the respective aldehydes and phosphonates by generalized Emmons-Horner procedure.28,29 In a typical procedure, respective benzyl bromides in DMF were refluxed with triethyl phosphite to obtain the corresponding phosphonates. The phosphonate thus prepared was subsequently taken in a dry round-bottomed flask containing suspension of sodium methoxide in freshly distilled and dry DMF. The mixture was magnetically stirred for 10 minutes to generate the corresponding anion to which was then slowly syringed-in the appropriate aldehyde solution in freshly dried DMF under inert (N2) conditions. The reaction mixture was stirred at ambient temperature for ~30 minutes. The progress of reaction was monitored by TLC (5% ethyl acetate/petroleum ether), and after the completion of reaction, the reaction mixture was quenched with brine and the organic material was taken-up in diethyl...
ther. The ether layer was dried with anhydrous sodium sulphate and subsequently ether was removed on a rotary evaporator. The solid compound obtained after the evaporation of diethyl ether was subjected to column chromatography to obtain the desired dienes. The dienes were further crystallized from chloroform-hexane.

1-(4-Nitrophenyl)-4-phenylbuta-1,3E-diene 1:

Yield 60%; mp 173-75°C. (Lit.: 178-79°C; UV THF): λ max (nm) (ε, 1 mol⁻¹·cm⁻³): 375 (56235); IR: 900, 1597, 1520, 1386, 970 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ 6.70 (1H, d, J = 15.2 Hz, C₆H₅-CH=CH-), 6.80 (1H, d, J = 15.1 Hz, p-NO₂-C₆H₄-CH=CH-), 7.00 (1H, dd, J = 15.2, 10.4 Hz, C₆H₅-CH=CH-), 7.13 (1H, dd, J = 15.3, 10.4 Hz, p-NO₂-C₆H₄-CH=CH-), 7.27-7.48 (5H, m, C₆H₅). 1597, 1535, 970 cm⁻¹ ; ¹H NMR (CDCl₃, 300 MHz): δ 8.20 (4H, AB quartet, J = 8.8 Hz, p-NO₂-C₆H₄-), 7.13 (1H, dd, J = 15.0, 10.6 Hz, p-NO₂-C₆H₄-CH=CH-), 6.79 (2H, d, J = 15.2 Hz, p-NO₂-C₆H₄-CH=CH-).

1,4-Di-(4-nitrophenyl)buta-1,3E-diene 2: Yield 50%; mp 264-265°C. (Lit.: 221-22°C; UV (MeOH)): λ max (nm) (ε, 1 mol⁻¹·cm⁻³): 385 (56234); R: 2940, 1597, 1535, 1510, 970 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ 8.21 (4H, AB quartet, J = 8.8 Hz, p-NO₂-C₆H₄-CH=CH-), 7.61 (4H, AB quartet, J = 8.8 Hz, p-NO₂-C₆H₄-CH=CH-), 2.19 (3H, d, J = 1.1 Hz, -Me).

1-Phenyl-2-methyl-4-(4-nitrophenyl)buta-1,3E-diene 3: Yield 40%; mp 172-73°C; UV (MeOH): λ max (nm) (ε, 1 mol⁻¹·cm⁻³): 367 (31622); IR: 2940, 1597, 1535, 1510, 970 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ 8.20 (2H, AB quartet, J = 8.9, 2.0 Hz, p-NO₂-C₆H₄-CH=CH-), 7.57 (2H, AB quartet, J = 8.8, 1.8 Hz, p-NO₂-C₆H₄-CH=CH-), 2.72-7.47 (5H, m, C₆H₅), 7.13 (1H, d, J = 15.3 Hz, p-NO₂-C₆H₄-CH=CH-), 6.79 (1H, s, Ph-CH=CH=CH=), 6.68 (1H, d, J = 15.9 Hz, NO₂-C₆H₄-CH=CH-), 2.16 (3H, J = 1.3 Hz, -Me).

1,4-Di(4-nitrophenyl)-2-methylbuta-1,3E-diene 4: Yield 55%; mp 221-22°C; UV (MeCN): λ max (nm) (ε, 1 mol⁻¹·cm⁻³): 375 (26915); IR: 2940, 1597, 1535, 1510, 970 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz): δ 8.22/7.49 (2H, AB quartet, J = 8.8, 2.4 Hz, p-NO₂-C₆H₄-CH=CH-), 2.85, 7.61 (2H, AB quartet, J = 8.8, 2.4 Hz, p-NO₂-C₆H₄-CH=CH-), 7.13 (1H, d, J = 15.5 Hz, p-NO₂-C₆H₄-CH=CH-), 6.79 (1H, s, p-NO₂-C₆H₄-CH=CH=) 6.79 (1H, d, J = 15.9 Hz, p-NO₂-C₆H₄-CH=CH-), 2.19 (3H, d, J = 1.1 Hz, -Me).

Acknowledgement

Research grant [37/7/95-R&D-II/559] from the Board of Research in Nuclear Sciences, Department of Atomic Energy, Government of India is gratefully acknowledged.

References


