



Remarks on the modelling of molecular binding forces in the Glue-DNT interaction

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The interactions between cyanoacrylate type of glue and model compounds for dinitrotoluene (DNT) and trinitrotoluene (TNT) are investigated using mainly spectroscopic techniques. Electrostatic fields emanating from dispersion and dipole interactions are thought to dominate the energy of interaction without any evidence for hydrogen bonding between the glue and any of the substrates. Vibronic spectral data strongly suggests polarization of the vibrational manifolds of the substrates. Careful analysis of nuclear magnetic resonance (nmr) spectral data reveals a good correlation between the nmr chemical shifts and the measured infrared shifts in the glue matrix. This profound observation may have implications for theoretical calculations of nmr chemical shifts.

Keywords: Vibronic polarization, Dispersion, Dipole, Infrared shifts, NMR chemical shifts, Glue matrix, 2,4-DNT/TNT

The nature of the intricate molecular interactions that bind molecules such as dinitrotoluene (DNT) and trinitrotoluene (TNT) substrates to cyanoacrylate type of glue are ordinarily obscure. The traditional approach describes these types of forces in terms of short range van der Waals forces of interaction including possibility of a significant hydrogen bonding component¹⁻⁵. There is sparse information concerning a detailed analysis of the interactions of glue with a substrate such as DNT at molecular level. In particular, chemical analysis of interaction of cyanoacrylate type of glue with a molecular surface such as DNT is non-existent in contemporary chemical literature.

There is growing interest in the kind and nature of chemical interaction between glue and DNT or even better TNT as a substrate. This interest emanates from the use of cyanoacrylate type of glue to bind TNT in military research work and practices. There is speculation that the glue adversely interacts with the TNT and possibly lowers its potency as an explosive. However, some counter claims suggest that the use of cyanoacrylate glue to bind TNT enhances its performance as an explosive. Evidently, in military and security circles the detailed molecular nature of the interaction between glue and TNT is currently a matter of some controversy⁶.

The use of TNT for research purposes is regulated under strict legislation; this creates a practical limitation on the availability and access to TNT. The application of

suitable model compounds with similar functional groups as in TNT is justified under the circumstance and appears to model the interaction of TNT with glue successfully. If additivity of substituents electronic effects on the aromatic ring is assumed⁷⁻⁹; benzene, nitrobenzene, toluene, 4-nitrotoluene and 2,4-dinitrotoluene (2,4-DNT) as model compounds together reproduce the substituents electronic effects for TNT satisfactorily. In particular, the closest model compound to TNT is 2,4-DNT which possesses the same functional groups as TNT: the aromatic ring, methyl substituent, two instead of three nitro substituents on the aromatic ring in the same comparable positions on the ring as for TNT.

This work focuses on spectroscopic techniques and molecular electronic calculations to elucidate the chemical nature of the DNT-glue interaction, and to assess the role of individual functional groups in this interaction such that inference can be made on the behaviour of TNT under similar chemical treatment¹⁰. Infrared and nuclear magnetic resonance (nmr) experiments entailed careful measurements of corresponding signals and their intensities for prominent functional groups in model compounds. The results are compared with the same functional groups for the substrates measured in the glue matrix.

The observed infrared shifts are correlated with corresponding nmr chemical shifts. Our findings reveal that for the same functional group, there is a definite

link between the non-dimensional infrared shifts and their nmr counterparts. This observation is intriguing because infrared phenomenon arises from vibrations of the bonds corresponding to the functional group; whereas, the nmr phenomenon concerns the detailed electronic environment of the magnetically active nuclei in the functional group¹¹. In essence, the infrared bands arise from vibrational motions of the bonds defining the functional groups, whereas, the nuclear magnetic resonance chemical shifts arise from differences in the electronic environments of the magnetically active nuclei defining the functional group in question. In other words, we observe an interesting correlation between molecular vibrations of the bonds and their corresponding electronic environments. This revelation is further illustrated by analysis of the low resolution vibronic spectra of the model compounds in the glue matrix; these appear devoid of the vibrational fine structural features as depicted for benzene in Fig. 1, and for other model compounds under Supplementary Data, Fig. S1-S3. In this instance, the presence of the glue suppresses the intensities of the vibrational fine structures corresponding to the breathing modes of the substrate molecule as shown for benzene and other model compounds in their excited electronic states. These observations suggest that the electronic transitions observed for the substrates molecules, are intimately linked to the vibrations of their skeletal framework. Thus, an empirical connection is implied between the intimate molecular electronic processes associated with a particular functional group and its vibrational motion.

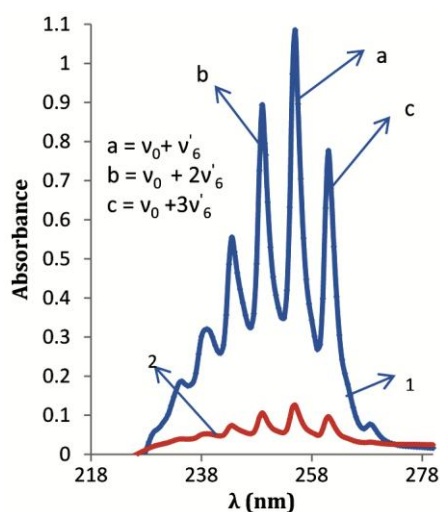


Fig. 1 — Low resolution absorption spectra of benzene in ethanol (0.05 mole%) without glue curve 1, in absolute ethanol (0.05 mole%) and with glue curve 2, in absolute ethanol.

In essence, our findings show that the glue interacts with model compounds such as benzene, 2,4-DNT and others, through dispersive interactions without forming any new chemical bonds or even discernible hydrogen bonds with the substrates. According to our calculations at B3LYP MP2 using diffused basis sets¹², these interactions appear to be dominated by electrostatic fields originating from dipole-dipole and dispersion forces and tend to polarize the vibrational motions corresponding to the functional groups with which they interact¹³. This polarization effect is observed in the infrared spectra of the whole range of model compounds, where diminished intensities and red shifts for prominent functional groups are consistently observed for measurements in the glue matrix.

Materials and Methods

Cyanoacrylate glue, 2,4-dinitrotoluene (2,4-DNT), deuterated chloroform (99.99% purity), toluene, nitrobenzene, 4-nitrotoluene, benzene and absolute ethanol were obtained commercially and all but ethanol used without further purification.

For infrared samples, a measured amount of a model compound such as 2,4-DNT (65% by weight) was placed in a watch glass with glue. These were dissolved in 3 drops of deuterated chloroform. The mixture was left for an hour in the fume hood to allow the chloroform to evaporate leaving a plasticized matrix of the model compound in glue.

Samples for the electronic spectral runs were prepared by making up 10 ml of 2,4-DNT (10^{-5} M) solution and 10 ml of glue (10^{-7} M) separately with re-distilled and dried up absolute ethanol. A mixture of 1 ml (0.05 mole%) from each of the two solutions was prepared and then siphoned into a 1 mm quartz cell using a syringe fitted with a hypodermic needle. In the case where the model compound was run alone, 1 ml of the substrate solution was mixed with 1 ml of the absolute ethanol instead of the glue solution.

The nmr samples were made up by dissolving a model compound such as 2,4-DNT (1 mole %) and glue (1 mole %) in deuterated chloroform and adding half a drop of deuterated benzene to stabilize the deuterium lock signal.

The infrared spectra for the sample matrices were collected on the Perkin Elmer FT-IR 2005 version 5.3 spectrophotometer by mounting a small amount of the solid sample delicately on the sample stage of the zinc selenide diamond crystal. In the case of neat glue samples, the glue was allowed to cure for 10 min on

the stage before spectra were collected. The crystalline solid samples of the pure model compounds were separately mounted on the stage to collect their spectra as well. The electronic spectra for 2,4-DNT were obtained in the near ultra violet on the Perkin Elmer Lambda 25 UV-visible double beam spectrophotometer, using 1 mm path quartz cells and operating in the 480-200 nm range. The nmr spectra were acquired on the Varian Mercury 400 MHz nuclear magnetic resonance spectrometer, using single scans for ^1H runs and some 250 scans for ^{13}C nuclei and setting all other acquisition parameters to their standard values in $\text{CDCl}_3/\text{C}_6\text{D}_6$ as solvents.

Results and Discussion

The nature of molecular forces of interaction between glue and the model compounds for TNT, such as 2,4-DNT, appear to be dipole-dipole with possible dispersion interactions involving the high electron rich functional groups of the glue molecule with those of the model compounds. Careful analysis of spectroscopic data for the interaction as presented in Table 1 suggests that the interaction involves intact functional groups without any concomitant bond breaking or forming processes involved. In Fig. 1, we present the low resolution vibronic spectra for the interaction of benzene with glue, as an example of the behaviour of the model compounds; further examples follow in the Supplementary Data as Fig. S1-S3. The in plane and out of plane skeletal vibrations of the benzene ring, the so called breathing modes of the aromatic ring are clearly visible even at this low resolution. The band is centred on 250 nm with the zero - zero ($\nu_{0,0}$) transition appearing at 265 nm, the band center remains unshifted even in the glue matrix.

The fine vibrational structures labelled a, b, and c, in Fig 1 correspond to the in plane skeletal vibrations of the ring in its excited state, the spike a corresponds to excitation of one quanta of vibration from the ground vibrational state, b to two quanta, c to three quanta and so on to complete the progression¹⁴⁻¹⁷. Evidently the vibrational progression is almost completely washed out in the presence of the glue, and the band intensity dramatically reduced. We believe that these results suggest that the interaction between the individual substrates; benzene, 2,4-DNT and the other model compounds with glue, manifests itself through a polarization of the vibrational manifold of the functional groups, as already alluded to with relevant references in the introduction. The electrostatic fields inducing the polarization appear to be of the dispersion and dipole-dipole kind and operate by constraining the functional groups or bonds to a more rigid geometry. The overall effect is to reduce the magnitudes of the electric dipole moments for the bonds undergoing vibrational motion. Consequently, the intensities are lowered and the vibrational bands shift to lower frequencies¹⁸.

Analysis of the nmr spectra leads to a similar conclusion. For example, in Table 1, the aromatic region reveals that the ring protons move up field in the glue matrix. We interpret this observation to mean that the interaction decreases the vibrational amplitudes of the bonds joining the nuclei thus affording the magnetically active nuclei enhanced contact with their immediate electron density. There is a good correlation between the glue matrix induced shifts observed in the infrared spectra of the 2,4-DNT and the corresponding relative chemical shifts measured in the nmr spectra as shown in Fig. 2. A

Table 1 — Measured infrared shifts (Γ), nmr chemical shifts (δ) for glue 2,4-DNT and calculated mutual relative shifts in the glue matrix at 300 K

DNT/ Glue $\Gamma^{\text{a}\pm}(1)^{\text{d}}$ (pph)	DNT/Glue $\delta^{\text{b}\pm}(1)$ (ppm)	DNT in glue Matrix $\Gamma^{\pm}(1)$ (pph)	DNT in glue Matrix $\delta^{\pm}(1)$ (ppm)	Rel. shifts $\Delta\Gamma $ (± 2) (pph)	Rel. shifts ^c $ \Delta\delta $ (± 1) (ppm)
0.330	1.281	C-H _{aromatic} 0.328	C-H _{3 glue} 1.29	0.0016	0.013
0.247	2.702	C-H _{glue} 0.263	C-H _{3 2,4-D} 2.66	0.017	0.040
- 0.2506	4.258	C=O _{ester} 0.257	H ₃ -C=O _{glu} 4.27	0.0063	0.012
-0.3077	6.572	C=C _{aromatic} 0.310	H -C _{glue} 6.59	0.0018	0.020
-0.3509	6.974	N-O _{assymmetric} -0.338	H ₂ -C-O _{glue} 6.99	0.013	0.019
-0.4199	7.606	N-O _{symmetric} 0.417	H-C _{aromatic} 7.58	0.0031	0.029
-0.4951	8.32	C-O _{ester} -0.501	H(4)-C-NO ₂ 8.29	0.0063	0.03
nil	8.73	nil	H(5)-C-NO ₂ 8.70	nil	0.03

^aInfrared shifts in pph for glue/2,4-DNT referenced with respect to averaged polystyrene frequency at 2330.2 cm^{-1} (1600.00 and 3060.34 cm^{-1})

^bNmr shifts in ppm of glue/2,4-DNT

^cRelative shifts are the differences between shifts for the 2,4-DNT/glue and corresponding shifts observed in the glue matrix

^destimated error in the last significant digit

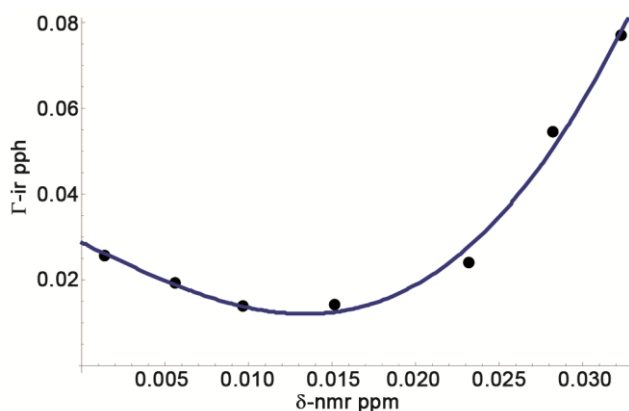


Fig. 2 — Plot of relative infrared (Γ pph) against nmr (δ ppm) shifts for 2,4-DNT in glue matrix. The functional relationship is given by $f(\Gamma) = 0.02878 - 1.872x + 3582.4056x^3 - 309758.7774x^5$, where x is the δ shift variable.

quintet relationship appears to reproduce the data points reasonably well in the high shift region.

These results are unexpected, however, the earlier conclusion is reaffirmed, and that is, the interaction involves electrostatic field perturbations of the bonds of the functional groups without formation or destruction of any bonds. In addition, this observation points to a direct linkage between the vibration of a bond corresponding to a functional group and its immediate electronic environment. The chemical shifts reflect the immediate electronic environment of the magnetically active nuclei of the functional group involved in the execution of a particular vibration. This result is intriguing; it demonstrates that the chemical shift of a nucleus in a bond is intimately connected to the vibration of the same bond. This implies that, theoretical models for the calculations of chemical shifts should factor in the vibrational motion of the bond(s) containing the magnetically active nuclei in question. The appropriate distribution function describing the immediate electron density of the vibrating nuclei if known, could improve the quality of theoretical calculations of chemical shifts. Theoretical calculations of chemical shifts are generally based on the assumption that the electrons move in a field of positive and rigid nuclei. It seems that calculations of chemical shifts premised on the Born Oppenheimer or adiabatic approximation are fundamentally inappropriate to reproduce the experimentally observed chemical shifts for nuclei in molecules.

Conclusions

The nature of the chemical interaction between the glue and DNT as a model compound for TNT is

dominated by dipole, dipole interactions and possible dispersive kinds of interactions between the bonds corresponding to the various functional groups of the substrate and the highly electron rich bonds in the glue functional groups. This interaction has important implications for both the vibrational motion of the bonds involved in the interaction and their immediate electronic environments. Therefore, it would seem that the use of cyanoacrylate type of glue to bind TNT for military operations or similar, should have little or no significant effect on the potency or thermodynamics of the substrate as an explosive.

Supplementary Data

Supplementary data associated with this article are available in the electronic form at [http://www.niscair.res.in/jinfo/ijca/IJCA 59A \(07\) 948-951_Suppl Data.pdf](http://www.niscair.res.in/jinfo/ijca/IJCA 59A (07) 948-951_Suppl Data.pdf).

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