Conformational Preference of 2,2'-Dinitrodiphenyl as Determined by Proton NMR Spectroscopy

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General Theory

Valence Shell Electron-Pair Repulsion (VSEPR) theory has been regarded for decades as a highly successful, albeit non-quantitative model used to predict molecular geometries.[1] The VSEPR model bases its conjectures on the simple modeling of repulsive forces between electron pairs surrounding a central atom. As two charges of the same sign—positive or negative—are brought closer together, each charge feels a greater and greater repulsive force due to the electric field produced by the other charge. Under simple electrostatic treatment[2]:

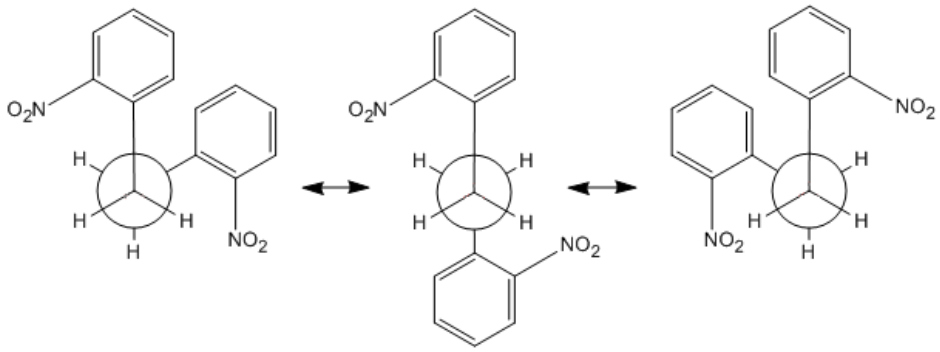
$$\vec{F}_{12} = q_1\vec{E}_2$$

This general idea can be likened to electron pairs, atoms, or substituents in a molecule: these differing electron "clouds" tend to orient themselves in a way so that the least amount of repulsion between their respective charges occurs.[3] By combining the predicted models of multiple central atoms, one can obtain a reasonable picture of conformation: how a more complex molecule will be oriented in space.

However, as with many theories, serious exceptions to the guidelines put forth by VSEPR theory exist. For example, the possible conformations of 1,2-Difluoroethane, depicted through Newman projections, are as such:

The VSEPR model in this case would predict the middle *anti* conformation as the most stable and most energetically favorable. However, experimental data has shown that the most stable conformer of this compound at room temperature is that of the possible *gauche* conformations[4] shown at the left and right, in direct conflict with this model. This concept is called the "gauche effect," in that the compound adopts a conformation with the most *gauche* interactions between substituents.[5] Numerous reasons could account for why this effect occurs. When analyzing the conformation of any compound, the task lies in explaining why this effect or any other perceived oddity happens. Within this framework, laboratory procedures is primarily geared toward determination of conformation, while actual "book research" is geared toward explaining the reasons for conformation.

The compound in question is 2,2'-Dinitrodiphenyl, with possible conformations:



1a **2** **1b**

The VSEPR model would predict the conformation resembling that of **2**, but it is possible that perhaps the most stable conformation is that of the **1a** or **1b** conformers, those exhibiting a gauche effect. There are many possible reasons for the occurrence of a more stable conformation of 2,2'-Dinitrodiphenyl with its substituent groups oriented *gauche* to each other.

First and foremost is the possibility of stabilization through hyperconjugation. This phenomenon occurs due to an interaction of the bonding and anti-bonding orbitals of two vicinal substituents of the ethane system.[6] In the compound of interest, each phenyl ring is greater stabilized through the donation of electron density into its ring, meaning it strongly attracts electrons being shared with electron-donating substituents, such as those from the alkyl group in this case, and so its anti-bonding acceptor orbital will interact with any coplanar carbon-hydrogen bonding donor orbital in the ethane molecule. In addition to this, the nitro group on each phenyl ring is strongly withdrawing, increasing the substituents' pull of possible donor electrons due to the depletion of electron density from the aromatic ring. Confirmation of the presence of a gauche effect within the molecule, a preferred conformer similar to **1a** or **1b**, could be explained by the presence of the two coplanar bonding-anti-bonding interactions, as opposed to the absence of this effect altogether in conformer **2**.

However, if the more stable conformer is more similar to that of **2**, a different explanation would be needed, and the VSEPR model would come back into play. In this case the important factor at work would simply be coulombic repulsion. Again, sites of high negative charge density exist in the phenyl rings. The repulsion of these two like charges would yield the preferential conformations as noted previously, with the least number of *gauche* interactions between substituents.

Another explanation of a more stable *anti* conformer would be because of steric hindrance. The nitrophenyl substituents are free to rotate around their bonds with the ethane backbone, but they are bulky, and would require more energy in order to rotate if they are situated *gauche* to each other, rather than *anti* due to the electron clouds experiencing a strong repulsion.[7] The *anti* conformation could subsequently relieve this steric congestion and yield an overall

decrease in energy, making it the preferred conformer.

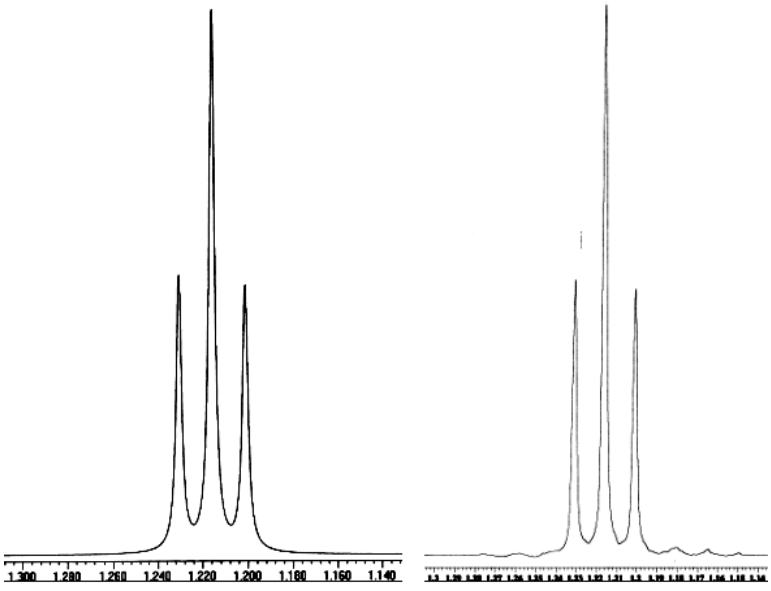
Finally, the importance of the solvent used to obtain NMR spectra is one other conformation-influencing factor that needs to be addressed. Initial laboratory work suggests that 2,2'-Dinitrodiphenyl dissolves in relatively non-polar solvents and aprotic polar solvents despite the large dipole moment associated with a nitro substituent on each phenyl ring. This is evidence already of possible conformational preference; this preference may still change due to interaction with the solvent.

In summation, there are many different and important effects to look for within analysis of the conformational preference of 2,2'-Dinitrodiphenyl, and confirmation of one preference would allow for subsequent further analysis of the effect of the placement of the nitro groups on the conformation of the molecule.

Procedure

2,2'-Dinitrodiphenyl, a solid in powder form, was purchased from TCI America with a purity of at least 98.0% measured by Gas Chromatography. Samples prepared for analysis by the JEOL 500 MHz NMR Spectrometer were approximately 0.2 M in concentration, requiring at least 41 milligrams of compound in 0.75 milliliters of solvent. If greater resolution in the NMR spectrum or better dissolution into the solvent was required, the concentration was reduced to approximately 0.1 M. ^{1}H spectra were taken at 25 °C in the deuterated solvents $CDCl_3$, Acetone-*d6*, DMSO-*d6*, and Acetonitrile-*d3*, each with TMS serving as a reference at 0.00 ppm. Each spectra acquired was comprised of thirty-two scans of approximately 8,000 data points, and the line broadening and zero-fill spectrum parameters were set to 0.0 Hz and 4, respectively. These latter two specifications were modified slightly to increase or decrease resolution of the spectrum if necessary.

All spectra obtained were then duplicated using an NMR spectra modeling software known as gNMR, which, when completely duplicated, yielded the vicinal and geminal *J*-values for the splitting patterns in question. For example, the duplicated spectrum of one peak of the compound 1-Ethyl-2-nitrobenzene is on the left, with the real spectrum on the right:



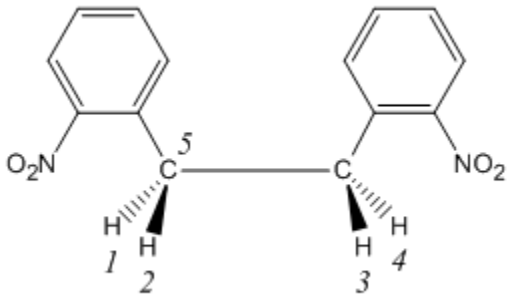
In this case, the splitting patterns of the carbon satellite peaks present in this compound were analyzed, resulting from the 1% probability of one of the carbons in the ethane backbone being a ^{13}C isotope. Their interactions with hydrogen atoms in the compound yield a splitting pattern with a frequency of ~150 Hz.

Lambda values used in the Altona Equation[8] are then left to be calculated for each of the substituents involved. Since the only substituent of the compound in question is the nitrophenyl group mentioned previously, ^{1}H NMR spectra of 99.0% 1-Ethyl-2-nitrobenzene, a liquid, was obtained and analyzed in each solvent analyzed previously using the same concentrations.

From all calculated *J*-values and Lambda values for 2,2'-Dinitrodiphenyl in each solvent, the Altona equation would be used to calculate the statistical weights of the possible conformations of the molecule. The Altona equation used in this part of the experimental data acquisition period is in the form of a programmed Mathematica worksheet.

Results

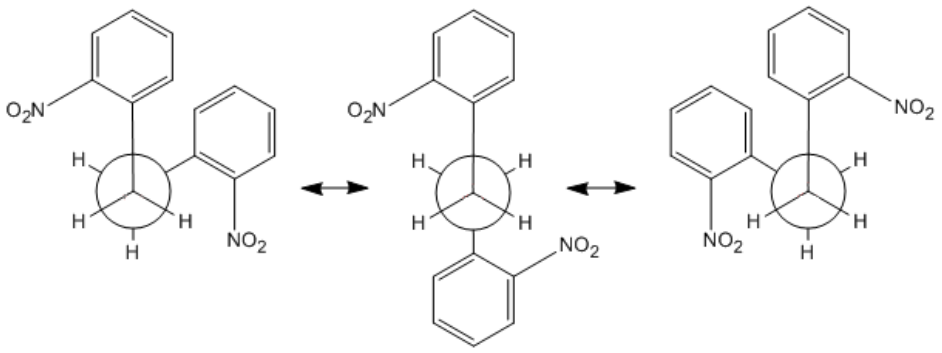
Conformational preferences of the compound in question, 2,2'-Dinitrodibenzyl, along with the *J*-values at 25 °C determined from the analysis in gNMR were found to be as follows, in order of increasing polarity of solvent:



Deuterated Solvent	***μ (D)*[9]**	***J_{13}, J_{24} (Hz)***	***J_{14}, J_{23} (Hz)***	***λ***	***Total % Gauche***
Chloroform	1.8963	10.47 ± 0.22	5.32 ± 0.25	0.82	29 ± 5
Acetone	2.88	10.22 ± 0.22	5.58 ± 0.24	0.48	36 ± 2
Acetonitrile	3.92519	9.28 ± 0.11	6.30 ± 0.11	0.48	48 ± 3
DMSO	3.96	9.10 ± 0.14	6.42 ± 0.12	0.48	50 ± 3

Discussion

Results for the *J*-values of the different coupling interactions present in 2,2'-Dinitrodibenzyl suggested initially that the conformation was more or less independent of the solvent; however, the differing lambda values coupled with this information yielded a large statistical difference in the percent *gauche* for each solvent. The data shows an increase in the overall conformation's *gauche* character as the polarity of the solvent increases, and by a rather significant amount. However, the total conformation still has a much larger *anti* character overall:



~15-25% **~50-60%** **~15-25%**

This preference is clearly explainable under the VSEPR model, although using this model may not yield all of the information possible. This finding may also substantiate the effect of steric hindrance — the bulky nitrophenyl groups make complete bond rotation in the molecule difficult. The results, in general, are nothing unexpected, but the dependence upon solvent polarity is something important to look into. It is perhaps possible that if the solvent is polar enough, and assuming the solvent can effectively dissolve the compound, the *gauche* conformer of 2,2'-Dinitrodibenzyl an become statistically favorable.

Conclusion

2,2'-Dinitrodibenzyl is significant in the realm of conformational studies in that the *J*-values determined between the different atoms on the ethane backbone deviate significantly enough from the expected value of ~7 Hz to expect a conformation either strongly *anti* or strongly *gauche*, as calculated through the use of the Altona equation. Hence, a specific conformational preference was to be expected for this compound, and it was exhibited: 2,2'-Dinitrodibenzyl is preferably *anti* in its conformation. However, the *gauche* character appears to increase with increasing solvent polarity, and this aspect warrants further investigation.

References

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