A Comparison of the Electron Density and Chemical Shift of Some 2,4-Dinitrophenylhydrazones

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The NMR chemical shift of the NH hydrogen is correlated with its electron density, as calculated by CNDO/2 method, for ten 2,4-dinitrophenylhydrazones. This gives a nearly linear plot, thus indicating that the chemical shift is largely decided by the electron density about the nucleus.

Scheme 1. (dnp = 2,4-dinitrophenyl).

In recent years there has been found a linear relationship between the NMR chemical shift of the nucleus and the electron density as calculated by semi-empirical molecular orbital methods. Good correlations are found for the case of ^{13}C nuclei.^{1,2} The ^1H shift has been correlated, on the basis of a formula developed by Fraenkel *et al.*,³ with the π electron density on the carbon atom to which the hydrogen atom is bound.⁴⁻¹⁰

In some cases the ^1H NMR shift has been correlated with the electron density of the hydrogen atom. Hamer *et al.*^{11,12} found a good correlation in their investigation of substituted styrenes. On the other hand, Roth¹³ found no correlation between the corrected chemical shift and the electron density about the hydrogen atom in the investigation of vinyl monomers. In other investigations reasonable to good results were obtained.¹⁴⁻¹⁷

RESULTS AND DISCUSSION

This investigation deals with ten 2,4-dinitrophenylhydrazones (DNPH's) whereof two make up a *syn/anti* isomer pair. The general form of the compounds is given as I, where either X or Y is a nitro group.

The configuration of the compounds (see below), the NH shift (δ), the electron density

(q_{H}) as calculated by the CNDO/2 method and NH stretch frequency (ν_{NH}) are given in Table 1.

Assignments of configuration. Compound 1 showed two NH peaks in the IR and two absorptions in the NH area in the NMR spectrum, thus indicating a mixture of both isomers. The band at lowest frequency¹⁸ and the absorption at lowest field¹⁹ may be ascribed to the *syn*-nitro isomer.

By comparing the NH position in the IR and NMR spectra of 2 and 3 with the positions found for compound 1, it was assumed that the *anti*-nitro isomer was present in each case.

The compound 4 showed exceptionally low NH frequency in the IR and showed a NH signal at low field in the NMR spectrum. The amide group is known²⁰ to form very strong intermolecular hydrogen bonds, and it was therefore assumed that the low NH frequency in the IR and the low field signal in the NMR spectrum were due to intra molecular hydrogen bonding from the amide group.

Compounds 5 and 6 existed in the form of both isomers in the ratio 9:1 as determined by the methyl signals in the NMR spectrum. Using Karabatsos' methods^{21,22} the isomer making the greatest contribution in each case

Table 1. Spectral data and electron density of 2,4-dinitrophenylhydrazones.

No.	Tentative assignment X ^a	Y ^a	δ_{NH} ^b	q_{H}	$\nu_{\text{NH}}/\text{cm}^{-1}$
1a	H	NO ₂	14.333	0.7530	3241
1b	NO ₂	H	11.666	0.8173	3283
2	NO ₂	CH ₃	11.000	0.8219	3302
3	NO ₂	CH ₂ CH ₃	11.166	0.8215	3304
4	NO ₂	CONH ₂	14.466 ^c	0.7543	3204 ^d
5	NO ₂	COCH ₃	14.000	0.7706	3160
6	NO ₂	CO ₂ CH ₃	13.499	0.7675	3204
7	NO ₂	NO ₂	13.466	0.7436	3222
8	NO ₂	F	11.350	0.8100	3261
9	NO ₂	Cl	11.283	0.8095	3267

^a X and Y refers to I. ^b ppm from internal TMS. ^c Uncertain by ± 0.2 ppm due to a very weak and broad signal. ^d Seems to come as an asymmetry of CH(arom) stretch frequency.

was determined to be the *anti*-nitro compound. No NH signal of the *syn*-nitro isomers was detected due to the low concentration.

Compounds 8 and 9 gave NH absorptions at high frequencies in the IR and at high field in the NMR spectrum and, compared with compound 1, it was assumed that these compounds existed as *syn*-halo isomers. This conclusion is supported by the fact that the *syn*-iodo isomer of 2-iodo-2-phenylhydrazonoacetonitrile could not be rearranged²³ into the *anti*-iodo isomer, which was expected to be the more stable form for steric reasons.

When the configurations were assigned, the chemical shift was plotted against the electron density as shown in Fig. 1.

In spite of a number of uncertain factors (see below) the points lie close to a straight line. The relatively large discrepancy, in the case of compound 7, may be the result of steric interaction between the nitro groups in the carbonyl moiety. As a result of this, one or both of the groups will be twisted somewhat out of the plane of conjugation. Calculations show that a twisting of the *syn*-nitro group of 30° out of the mesomeric plane leads to an increase in electron density such that the point for this conformer lies on the line (7', Fig. 1).

The scatter of the points about the line can be the result of a series of factors: failure in the description of the real geometry, non-linear electric field effects,^{24,25} bond anisotropic effects from groups in the neighbourhood of the NH hydrogen,²⁶ overestimation of charge dipole sigma polarization²⁷ and solvation effects as the shifts are not corrected to the gas phase due to the low solubility of the compounds. Such correction to the gas phase does not, however, necessarily lead to a better result.⁸

Nelson *et al.*² suggest that the geometry is a critical factor, since small differences in geometry (*ca.* 0.02 Å) can lead to "discrepancies comparable to the calculated charge densities". In the present work a different set of coordinates was used in addition to the coordinates determined by the COORD program (see experimental). These were found by geometrical constructions from standard bond lengths and

Fig. 1. Correlation of the NH proton shift (δ) vs. the electron density (q_{H}) as calculated by the CNDO/2 method. The equation of the line is: $\delta = 51.86 - 49.7q_{\text{H}}$ where S.D. in the constant is 0.95, in the slope 3.6 and in δ 0.266.

angles. Differences between the two sets were at most 0.07 Å, and this led to differences in electron density about the NH hydrogen of up to 0.0362. The points were still grouped around a straight line and had a correlation coefficient of 0.97. This suggests that the difference in geometry is not critical with respect to the linearity of the correlation, even if the individual points are somewhat changed in position.

Bond anisotropic effects are difficult to judge quantitatively as a result of the uncertain data available for bond susceptibilities.²⁸

Linear regression (compound 7 excluded) gave $r=0.98$. The slope of the line is 3060 Hz/electron or 50 ppm/electron. This is higher than the previously calculated scale-factors of 26.6 ppm/electron for the shielding of a proton in the hydrogen molecule,²⁹ and 17.8 ppm/electron for diamagnetic shielding in a hydrogen atom.³⁰ Sebastian and Grunwell¹⁵ found a slope of 23.4 ppm/electron, while Hamer *et al.*^{11,12} found values from 17.0 ppm/electron to 23.2 ppm/electron.

However, the slope of the line is sensitive to changes in geometry. Thus a value of 30.6 ppm/electron was found when using the second coordinate set (see above).

Lazzaretti and Taddei¹⁴ give no slope values in their work, but by using their data it is possible to calculate a slope of about 130 ppm/electron in the series where the substituents belong to the second row of the periodic system. This large difference from the previously stated values can indicate that the semi-empirical method of del Re which Lazzaretti and Taddei used, underestimates charge differences.

The investigation of Sterk and Holzer¹⁶ shows considerable differences in slope values as various semi-empirical methods are employed. In their correlation A1 they found a slope of 12.0 ppm/electron as calculated by MINDO/2, 13.9 ppm/electron by INDO, 1.9 ppm/electron by EHT and 21.4 ppm/electron as calculated by CNDO. The CNDO value is in excellent agreement with the previously stated values.^{11,12,15,29,30}

In the work of Ohkubo *et al.*¹⁷ no slope values are given, but one could calculate values ranging from ~12 ppm/electron to ~200 ppm/electron for the OH proton. Ohkubo *et al.* give no explanation of this great variation.

On the basis of the good correlation and the reasonable value of the slope, the conclusion is drawn that the chemical shift of the NH proton is mainly determined by its electron density.

An interesting aspect of the correlation is that it may be used in *syn/anti* assignment of hydrazones where a relatively large electron density variation about the NH hydrogen atom takes place, *cf.* compounds 1a and 1b. This will be further investigated in a following paper.

EXPERIMENTAL

Synthesis of the compounds $\text{NO}_2\text{--CH}_2\text{--X}$ ($\text{X}=\text{H}, \text{CH}_3, \text{CH}_2\text{--CH}_3, \text{CONH}_2, \text{COCH}_3, \text{CO}_2\text{CH}_3, \text{NO}_2$). Nitromethane, nitroethane and 1-nitropropane were obtained from commercial sources (Fluka A.G.). The various steps in the synthesis of nitroacetamide,^{31–33} nitroacetone,^{34,35} methyl nitroacetate^{31,32} and dinitromethane^{36,37} are described in the literature.

Diazo couplings. For $\text{X}=\text{H}, \text{CH}_3$ and CH_2CH_3 , a procedure given in Organic Reactions³⁸ was followed. In all other cases the method described by Juvvik and Solheim³⁹ was used. The hydrazones so formed were purified by recrystallization from a water/acetic acid mixture, or by preparative TLC.⁴⁰

Compounds 8 and 9 were synthesized by allowing 7 to react with excess of the respective halogen acid in a dimethyl sulfoxide:water (2:1, v:v) solution. At the completion of the reaction the mixture was diluted with water and the product extracted with ethyl acetate and purified by preparative TLC.

Infrared spectra of the compounds dissolved in tetrachloroethylene (E. Merck, Uvasol) in 4.00 cm cells were obtained on a Unicam SP 200G instrument.

NMR spectra of the compounds dissolved in trichloroacetonitrile (EGA, 99 % purity) were recorded on a JEOL Minimar 60 or a JEOL HNM-C-60H high resolution instrument, both operating at 60 MHz. The position of the various signals was measured by a Hewlett-Packard 5326 A frequency counter in the frequency sweep mode and internal lock to the TMS signal.

The quantum mechanical calculations were performed using a modified CNDO/2 program.⁴¹ The program uses *s* and *p* Slater orbitals for all atoms except hydrogen where only the *s* orbital is used. All parameters were taken from the original papers.^{42,43}

Molecular geometry. On the basis of X-ray crystallographic data,^{44–46} the bond length N–N was set at 1.40 Å. The element –NH–N=C was considered to be co-planar with the 2,4-dinitrophenyl ring.^{44,45} The bond length

C-Cl was set at 1.73 Å.⁴⁷ In all other cases standard bond lengths and angles were used.⁴⁸ The actual transformations to coordinates were performed by the program COORD.⁴⁹

The CNDO/2 and the COORD calculations were undertaken on a Univac 1110 computer.

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