## 88. *Nuclear Magnetic Resonance Shielding Parameters, and the Structure of Diazoalkanes.*

### By A. Ledwith and Edwin C. Friedrich.

The nuclear magnetic resonance shielding parameters for twelve diazo-alkanes are reported and the effect of substituents on the electron density around the α-proton is considered in relation to structure.

DIAZOALKANES, $RR'CN_2$, are best represented by the canonical structures (I) and (II), and therefore are able to react with electrophilic reagents at the carbon or nitrogen atom of the diazo-group depending on whether structure (I) or (II), respectively, contributes

$$\text{(I) } RR'C=N^+=N^- \longleftrightarrow RR'C^--N^+\equiv N \text{ (II)}$$
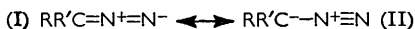
most to the resonance hybrid.[1] Infrared [2,3] and electronic absorption spectroscopy [3] have helped to characterise the C–N–N chromophore. If other effects could be accounted for, nuclear magnetic resonance (n.m.r.) spectroscopy might be expected to provide a better estimate of the relative contributions of the two forms since they would give different electron densities around the substituents R and R'.

The Table shows the chemical shifts and relevant $\tau$ values for a series of diazoalkanes and suitable reference molecules. Values for the aromatic ring protons are measured to the geometrical centre of the entire resonance signal and not necessarily to the highest peak. Experiments with undiluted liquid diazoalkanes and with solutions in various solvents showed no significant solvent effect on the chemical shifts.

Diazomethane shows considerable carbanionic character [*i.e.*, (II; R = R' = H)], as shown by the increased shielding, causing a shift to higher field, of the methylene hydrogen atoms when compared with allenic, olefinic, or aldehydic protons.[4] It is possible, however, that the increased shielding of the α-hydrogen atoms in diazomethane or a monosubstituted diazomethane may be due in part to the diamagnetic anisotropy of the diazo-group, similar to that found in acetylenes [5] and nitriles.[6] The α-proton in diazoethane has a

[1] Huisgen, *Angew. Chem.*, 1955, **67**, 439; Zollinger, " Azo and Diazo Chemistry," Interscience Publ., Inc., New York, 1961.

[2] Fahr, *Annalen*, 1958, **617**, 11; 1961, **638**, 1; Yates, Shapiro, Yoda, and Fugger, *J. Amer. Chem. Soc.*, 1957, **79**, 5766.

[3] Ledwith and Friedrich, unpublished work.

[4] (*a*) Jackman, " Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon, London, 1959; (*b*) Pople, Schneider, Bernstein, " High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., New York, 1959.

[5] Whipple, Goldstein, and Stewart, *J. Amer. Chem. Soc.*, 1959, **81**, 4761.

[6] Reddy, Goldstein, and Mandell, *J. Amer. Chem. Soc.*, 1961, **83**, 1300.

| Diazo-compound | Solvent | Chemical shift (c./sec.) * | $\tau$ (p.p.m.) | Complexity of signal |
|---|---|---|---|---|
| $CH_2N_2$ | $CCl_2F \cdot CF_2Cl$ | 123 | 6·92 | |
| $CH_3 \cdot CHN_2$ | $CCl_2F \cdot CF_2Cl$ | $\alpha$ 129 | 6·78 | |
| | | $\beta$ 68 | 8·30 | Doublet |
| $CH_2{=}CH \cdot CHN_2$ | $CCl_4$ | $\alpha$ 184 | 5·42 | Multiplet |
| | | $\beta$ 131 | 6·72 | Quartet |
| | | $\gamma$ 43 | 8·93 | Triplet |
| $N_2 \cdot CH \cdot CO_2Et$ | Homog. | $\alpha$ 199 | 5·04 | |
| $N_2CH \cdot CO_2Me$ | ,, | $\alpha$ 199 | 5·04 | |
| $\begin{matrix} CH{=}CH \\ \mid \quad\quad {>}CN_2 \\ CH{=}CH \end{matrix}$ | $CCl_4$ | $\alpha$ 265 | 3·38 | Quartet |
| | | $\beta$ 235 | 4·14 | Quartet |
| $Ph \cdot CHN_2$ | $CCl_4$ | $\alpha$ 184 | 5·42 | |
| | | ar 276 | 3·10 | Multiplet |
| | Homog. | $\alpha$ 182 | 5·47 | |
| | | ar 278 | 3·06 | Multiplet |
| $Ph \cdot CHO$ | $CCl_4$ | $\alpha$ 400 | 0·01 | |
| $Ph \cdot CH{=}N \cdot NH_2$ | $CCl_3$ | $\alpha$ 212 | 4·71 | |
| $Ph_2CN_2$ | $CH_2Cl_2$ | 291 | 2·74 | Singlet |
| $(p\text{-}MeO \cdot C_6H_4)_2CN_2$ | $CH_2Cl_2$ | ar 278 | 3·06 | Quartet |
| | | MeO 147 | 6·32 | |
| 9-Diazofluorene | $CH_2Cl_2$ | 292 | 2·70 | Multiplet |
| | | 311 | 2·20 | Multiplet |
| Cf. Terminal methylene proton | | | 5·45 | Ref. 4a |
| Terminal allenic proton | | | 5·70 | ,, |
| Acetylenic proton | | | 7·75 | ,, |
| Aldehydic proton | | | 0·50 | ,, |

\* Chemical shifts were measured at 40 Mc. with hexamethyldisiloxane as internal standard. The values shown have been corrected to tetramethylsilane as reference by addition of 2·4 c./sec. to those measured.

chemical shift similar to that for the protons in diazomethane, and diazoethane is best represented as (II; R = Me, R' = H). The alternative form (I) would be expected to have a contribution from structures such as $CH_3 \cdot CH^+{-}N{=}N^-$ and this would result in deshielding of the $\beta$-protons. In fact the shielding of the $\beta$-protons in diazoethane is normal for a methyl group attached to an unsaturated system.

The chemical-shift measurements appear to show that vinyldiazomethane (3-diazo-prop-1-ene) has most carbanion character, especially at the $\gamma$-carbon atom where the methylene protons are found at $\tau$ 8·93. Normally in allylic derivatives [4] the $\gamma$-methylene protons have $\tau$ ~5·5, but in allylic Grignard reagents the carbanionic methylene protons give a signal at higher fields.[7] For vinyldiazomethane, therefore, it is possible that canonical structure (II) is further stabilised by the contributions from the allylic resonance forms (IIa and b).

(IIa) $CH_2{=}CH{-}CH^-{-}N^+{\equiv}N \longleftrightarrow ^-CH_2{-}CH{=}CH{-}N^+{\equiv}N$ (IIb)
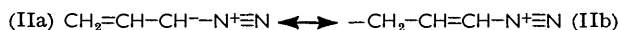
The relative chemical shifts of the $\alpha$-, $\beta$-, and $\gamma$-protons would then indicate that form (IIb) predominates, although the signal due to the $\alpha$-proton is no doubt considerably influenced by the electropositive diazonium substituent. It is possible, however, that

(Ia) $CH_2{=}CH{-}CH{=}N^+{=}N^- \longleftrightarrow$  (IIIb)
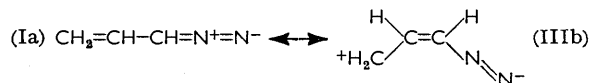
the very large shielding of the $\gamma$-methylene protons is due in part to the contribution of a resonance structure (IIIb) derived from (Ia), in which vinyl diazomethane has a

[7] Nordlander and Roberts, *J. Amer. Chem. Soc.*, 1959, **81**, 1769; 1961, **83**, 494; see also Johnson, Weiner, Waugh, and Seyferth, *ibid.*, p. 1306.

*cis*-structure. The observed shielding would then be explained if the anisotropic shielding effect of the N=N bond were similar to that of a C=C or a C=O bond, *i.e.*, positive shielding in conical regions extending above and below the plane of the double bond;[4] consequently, the γ-methylene protons in this *cis*-configuration would be shielded considerably. Further, a *cis*-structure such as (IIIb) could account for the spontaneous isomerisation of vinyldiazomethane to pyrazoline.[8] This rough estimate of the electron density in vinyldiazomethane is supported by a detailed analysis of the fine structure present in the n.m.r. spectrum and by ultraviolet- and infrared-spectral analyses.[9] Resonance stabilisation of type (I) is possible in phenyldiazomethane, namely:
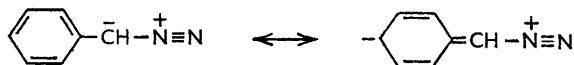


The chemical shift of the α-hydrogen atom (τ 5·42) is identical with that of vinyldiazomethane and appreciably different from that of the α-hydrogen atom of benzaldehyde (τ 0·01) and its hydrazone (τ 4·71). Stabilisation of the carbanionic form (II) can also be expected for diazo-esters:

$$N{\equiv}N^{+}{-}C{\cdot}H{\cdot}CO_2R \longleftrightarrow N{\equiv}N^{+}{-}CH{=}C(OR){-}O^{-}$$

and this is borne out by the chemical shifts of the α-hydrogen atoms in methyl and ethyl diazoacetate, which are comparable with those for the α-hydrogen atoms of the molecules discussed above.

When considering the chemical shifts of the ring-protons of diaryldiazomethanes, it is reasonable to assume that a *p*-methoxy-substituent will stabilise structure (I), just as it stabilises a triarylmethyl carbonium ion, and this could be one reason why the ring-protons of the triphenylmethyl carbonium ion are less shielded than the ring-protons of the tri-*p*-methoxy-ion.[10] For diazo-compounds there is a similar effect, the ring protons in di-*p*-methoxyphenyldiazomethane giving signals at a higher field than do those of diphenyldiazomethane. The ring-protons of 9-diazofluorene are the least shielded of all the diazoalkanes investigated, and for this molecule we should expect structure (II) to predominate:
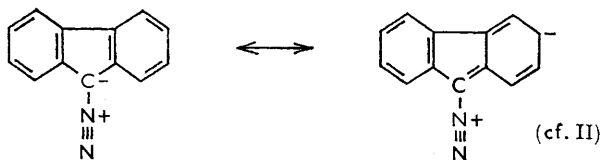


In this case, however, the spectrum is resolved into two multiplets separated by 19 c./sec. and having areas in the ratio 6 : 2. The larger peak is at higher field, so we have provisionally assigned the minor peak to the 1,8-ring-protons which are most likely to be deshielded by the diazonium substituent. Similar effects would be expected for diphenyldiazomethane, but it is significant that this molecule gives only sharp unresolved signals at 40 and 60 Mc; apparently the chemical shifts of the ring protons are here virtually identical, in contrast with the chemical-shift differences between the corresponding ring protons in benzophenone and its hydrazone[3] where the *ortho*-protons are presumably to some extent deshielded.

Diazocyclopentadiene is often considered as a prototype of the non-benzenoid aromatic system[11] because of the possible existence of a resonance-stabilised cyclopentadienyl

[8] Wilds and Meader, *J. Org. Chem.*, 1948, **13**, 763.
[9] Feeney and Bell, University of Liverpool, unpublished work.
[10] Moodie, Connor, Stewart, *Canad. J. Chem.*, 1959, **37**, 1402.
[11] Doering, Symposium on Theoretical Organic Chemistry (Kekulé Symposium), Butterworths, London, 1959, p. 35.

anion derived from structure (II).   The n.m.r. spectrum of this compound is resolved into two equivalent, but unsymmetrical, quartets, corresponding to an $A_2X_2$ system [4b] with $J_{AX} + J_{AX'} \sim 7$ c./sec.   The chemical shift of the β-ring-protons ($\tau$ 4·14) is comparable
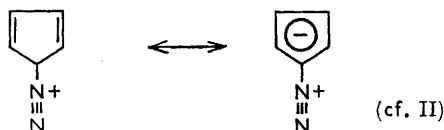


with that of the ring-protons in cyclopentadienyl-lithium, -sodium, and -magnesium [12] ($\tau$ 4·0—4·5) where the cyclopentadienyl anion also occurs.   Consequently it seems clear that diazocyclopentadiene has very little contribution from structure (I) and possess almost complete carbanion character in the ring.*

In summary, the n.m.r. shielding parameters are in reasonable accord with the usual nucleophilic and carbanion-like character of diazoalkanes, exceptions being likely in the case of the diazomethanes that possess substituents which stabilise the carbonium ion form.

The $\tau$ values for the α-protons fall in the range 5·0—6·9.*

*Experimental.*—Diazomethane,[15] diazoethane,[16] and vinyl diazomethane [17] were prepared in a pure state by the action of the monosodium derivative of ethylene glycol on the corresponding *N*-nitrosourethanes, as described previously.[17]   The diazoacetic esters were obtained by the action of nitrous acid on the appropriate glycine ester hydrochloride.[18]   All the aryldiazoalkanes were prepared by oxidation of the corresponding hydrazones by mercuric oxide in the conventional manner.[19]   Diazocyclopentadiene was kindly supplied by Dr. R. Partos of the University of California, Los Angeles 24.

N.m.r. spectra were obtained by using a Varian 4300B spectrometer operating at 40 Mc/sec. Concentrations of diazoalkanes varied from 5 to 30% w/v depending on the signal : noise ratio.

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* Since this work was completed, Cram and Partos [13] have independently confirmed this assignment for diazocyclopentadiene and its 2-nitro-derivative.   In addition, for ω-diazoacetone in carbon tetrachloride,[14] the α-proton has $\tau$ 4·82.

[12] Fraenkel, Carter, McLachlan, and Richards, *J. Amer. Chem. Soc.*, 1960, **82**, 5846.
[13] Cram and Partos, *J. Amer. Chem. Soc.*, 1963, **85**, 1273.
[14] Dahn, Danzel, Merbach, and Gold, *Helv. Chim. Acta*, 1963, **46**, 994.
[15] Gutsche, " Organic Reactions," Wiley and Sons, New York, Vol. VIII, p. 364.
[16] Hurd and Lui, *J. Amer. Chem. Soc.*, 1935, **57**, 2656; Nordlinger and Acree, *Amer. Chem. J.*, 1910, **43**, 381; Adamson and Kenner, *J.*, 1935, 286.
[17] Bawn and Rhodes, *Trans. Faraday Soc.*, 1954, **50**, 934.
[18] Grundmann and Ottman, *Annalen*, 1953, **582**, 173.
[19] Gutsche and Johnson, *J. Amer. Chem. Soc.*, 1955, **77**, 5933; Miller, *J. Org. Chem.*, 1959, **24**, 560.