^{13}C and ^{15}N Nuclear Magnetic Resonance Parameters of Ethyl Diazoacetate

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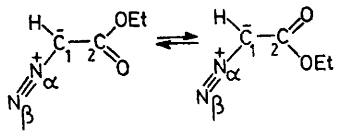
Summary ^{15}N Chemical shifts of both singly labelled and the doubly labelled isotopic modifications of ethyl diazoacetate accord with qualitative expectations; the ^{13}C—^{15}N and ^{15}N—^{15}N coupling constants compare with calculated values which demonstrate the dominance of the Fermi contact term and the importance of the nitrogen lone pair.

INTEREST in the mechanisms of nuclear spin–spin coupling, the availability of more reliable and sophisticated computational methods,[1] and the recent appearance of closely related studies[2,3] whose results differ in some detail from our work, prompted us to examine all the ^{15}N isotopic modifications of ethyl diazoacetate (**1**), an accessible model for diazo-type structures. The materials were synthesized from appropriate combinations of 95%-enriched and unenriched sodium nitrite and ethyl glycinate; ^{15}N and ^{13}C spectra were determined on a JEOL PS/PFT-100 spectrometer at room temperature (*ca.* 20 °C) and at −50 °C. At the latter temperature the two conformational isomers, *Z*-(**1**) and *E*-(**1**), are frozen out.[4] The room-temperature ^{13}C shifts agree with reported values for the methyl[5a] and ethyl[3] esters. The high-field position of the C(1) resonance has been attributed[5a] to increased electron density at that site. It may be relevant, however, that the terminal carbon resonance of allene, which is of the same symmetry as C(1) in (**1**), lies *ca.* 40 p.p.m. to higher field than that of ethene.[5b] Thus factors other than charge must influence the chemical shift. That expected electronic charge does not necessarily preponderate in systems of this type is clear from the nitrogen shifts. While our values agree numerically with those of Mason and Vinter,[2] their assignments must be reversed, as indicated by our experiments with singly labelled materials. In addition, our values differ by *ca.* 50 p.p.m. from those of Albright and Freeman.[3] That ours are correct is evident from the position of the nitromethane reference signal, which is exactly in the region of N(β) in the low-temperature spectra (Figure). Since the chemical shift difference between the two nitrogen nuclei is the same in both studies, the most likely explanation for the discrepancy may be aliasing of the positions of the signals because of inappropriate choices of spectral width and offset. The 116 p.p.m. upfield position of the positively polarized N(α) parallels the difference between nitriles and nitrile oxides or isocyanides,[6] and the difference between pyridines and pyridinium ions.[6,7] In each case the high-field resonance position may be associated with removal of the lone pair from nitrogen, which reduces the paramagnetic component of the chemical shift. The greater importance of this term in the chemical shift expression for N(β) probably accounts for the greater sensitivity of the N(β) *vs.* N(α) shifts at low temperature. The assignment of the low-temperature resonances are tentatively based on the assumed parallelism with the behaviour of the methine proton.[4] The room-temperature ^{15}N spectrum of the doubly labelled material displayed a sharp doublet for N(α) but a broad signal for N(β). From the chemical shift and coupling constant values, the activation free energy for *Z–E* isomerization, calculated[8] to be 14·1 kcal mol^{-1}, is in reasonable agreement with the reported value[4] of 13·3 kcal mol^{-1}.



Z-(1) *E*-(1)

The one-bond C–N coupling constant (Table 1) agrees remarkably well with that (20·6 Hz) predicted on the basis of the relationship[9] $S_N S_C = 80\ ^{1}J_{\text{NC}}$. That it should is further evidence for our rules regarding the predominance and nature of the Fermi contact term in CN coupling.[1b] Similarly, $^{2}J_{\text{NC}}$ agrees with that (3·9 Hz) anticipated from the corresponding value of $^{2}J_{\text{NC}}$ in acetonitrile (3·0 Hz)[10] when the differences in carbon hybridization are considered. That the Fermi contact term dominates the orbital and spin dipolar parts of the CN coupling is apparent from the calculated INDO coupled Hartree-Fock values (Table 2), carried out for convenience on the *Z* form of the methyl ester. Of the values in Table 1, perhaps the most interesting are $^{1}J_{\text{NN}}$, whose values, 5·62 and 5·13 Hz, we tentively assign to the *E* and *Z* isomers. The calculations indicate that $^{1}J_{\text{NN}}$ is dominated by the Fermi contact term, whose negative sign appears to arise from a negative contribution of the *sp*-hybridized lone-pair orbital on N(β), which opposes the positive contribution expected from the localized N(α)–N(β) bonding orbital. An argument of this type was shown recently to explain the well known one-bond lone-pair effect on C–N couplings.[1] Furthermore, the relative signs of the three contributions and the total $^{1}J_{\text{NN}}$ are the same as the corresponding 'reduced' values for $^{1}J_{\text{C}\equiv\text{N}}$ in acetonitrile, but in the latter case the orbital and dipolar terms are predominant. It should be noted that the only similar N≡N species whose coupling constant is known is the titanium complex of Bercaw *et al.*,[11] for which $|^{1}J_{\text{NN}}| = 7 \pm 2$ Hz.

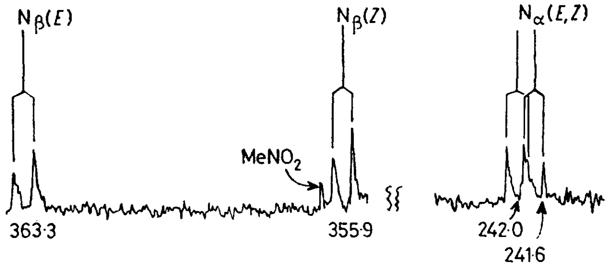


FIGURE. ^{15}N resonances of [^{15}N$_2$]diazoacetate at −50 °C. The numbers are the chemical shifts in p.p.m. from ammonium chloride.

Finally, our results strongly suggest that a simple relationship between N–N couplings and hybridization will not exist.

TABLE 1. ^{13}C and ^{15}N Chemical shifts and coupling constants of ethyl diazoacetate[a]

	20 °C	−50 °C
δ[C(1)]	45·87	44·2, 46·2
δ[C(2)]	166·46	166·1, 166·6
δ(CH$_2$)	60·82	60·9, 61·3
δ(CH$_3$)	14·50	14·5
δ[N(α)]	242·69	241·6, 242·0
δ[N(β)]	358·92	355·9 (*Z*), 363·3 (*E*)
^{1}J[C(1)N(α)] ..	21·36	23·2[b], 20·8[c]
^{2}J[C(1)N(β)] ..	3·66	3·2
^{2}J[C(2)N(α) ..	1·2	—
^{1}J[N(α)N(β)] ..	5·65	5·62 (*E*), 5·13 (*Z*)
^{1}J[C(1)H] ..	203·3	—
^{2}J[N(α)H] ..	2·8	—
^{3}J[N(β)H] ..	1·0	—

[a] ^{13}C Chemical shifts in p.p.m. relative to internal Me$_4$Si. ^{15}N Chemical shifts, measured with respect to external ^{15}NH$_4$Cl in 1M HCl at 20 °C, and external Me^{15}NO$_2$ at −50 °C, are reported relative to ^{15}NH$_4$Cl: $\delta(\text{NH}_4) = \delta(\text{MeNO}_2) + 355{\cdot}3$. Coupling constants are in Hz, estimated error ±0·2 Hz. [b] δ 44·2 signal. [c] δ 46·2 signal.

TABLE 2. Calculated N–N and C–N coupling constants[a,b]

	Fermi contact	Orbital	Dipolar	Total
^{1}J(NN) ..	−6·6	0·8	2·7	−3·1
^{1}J[N(α)C] ..	−13·8[c]	1·1	0·1	−12·5
^{2}J[N(α)C] ..	1·3	0·0	0·0	1·3
^{2}J[N(α)H] ..	1·0	—	—	1·0
^{2}J[N(β)C] ..	−2·1	0·9	−1·3	−2·5
^{3}J[N(β)C] ..	2·4	0·2	0·7	3·3
^{3}J[N(β)H] ..	−0·1	—	—	−0·1

[a] The relevant geometrical parameters used were: R(NN) = 1·10, R[CN(α)] = 1·34, R[C(1)C(2)] = 1·42, R[C(1)H] = 1·08 Å. Except for the methyl group the molecule was planar with angles of 120° about C(1) and C(2) and 180° about N(α). [b] The spin–spin coupling parameters employed were, in units of a_0^{-3}: $S_{\text{H}}^{2}(0) = 0{\cdot}318$, $S_{\text{N}}^{2}(0) = 4{\cdot}77$, $\langle r_{\text{N}}^{-3}\rangle = 3{\cdot}101$ for CH and NN couplings, For CN couplings, the single-bond values of ref. 1 were used. [c] This result agrees with ref. 3, which used slightly different spin densities and which suggested the geometry employed here. The corresponding calculation for diazomethane, however, diverges.

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