Carbon-13 Nuclear Magnetic Resonance Study of Carbon Suboxide

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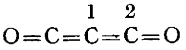
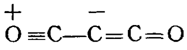
Summary The carbon-13 n.m.r. spectrum of carbon suboxide has been recorded and a remarkably high field resonance observed for the central carbon atom.

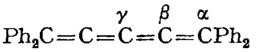
THE electronic structure and geometry of carbon suboxide (**1**) has been the subject of much discussion.[1–4] It has been suggested that the low frequency of the bending mode at the central carbon atom (63 cm^{-1})[1] arises from a low C–Cπ bond population and very high electron density on this atom.[2] In view of the sensitivity of ^{13}C n.m.r. spectra to electronic structure, providing similar molecules are compared,[5] we decided this might be a useful technique to obtain information on (**1**).


$$\mathrm{O{=}C{=}\overset{1}{C}{=}\overset{2}{C}{=}O}$$

(**1**)


$$\mathrm{\overset{+}{O}{\equiv}C{-}\overset{-}{C}{=}C{=}O}$$

(**2**)


$$\mathrm{Ph_2C{=}C{=}\overset{\gamma}{C}{=}\overset{\beta}{C}{=}\overset{\alpha}{C}Ph_2}$$

(**3**)

Compound (**1**) was prepared by the dehydration of malonic acid, collected in a liquid-nitrogen trap, and subsequently dissolved in $CDCl_3$ at *ca.* −50 °C. The ^{13}C n.m.r.-spectrum was obtained at −40 ± 1 °C on a VarianXL-100-15 spectrometer operating in the FT mode at 25·16 MHz using Me_4Si as an internal standard. A paramagnetic relaxation reagent, $[Cr(acac)_3]$[6] was added to shorten the spin-lattice relaxation times (T_1) of the carbon nuclei; comparison with a spectrum taken without $[Cr(acac)_3]$ using a 50 s pulse delay showed no chemical shift changes. The spectrum of (**1**) is shown in the Figure.

The most noteworthy feature of this spectrum is the extremely high-field position of the central carbon atom C-1; at −14·6 p.p.m. it is one of the most shielded carbon atoms reported to date. In view of the unusual structure of (**1**), however, it is difficult to find model systems suitable for the comparison of ^{13}C data. *A priori* the *sp*-hybridized C-1 would be expected to appear at higher field than the analogous terminal carbon atom (sp^2) of keten.[7] Moreover, the very high electron density on this carbon atom which would be expected on the basis of mesomeric structures such as (**2**), and is predicted by CNDO/2,[2] EHT,[2] and *ab initio*[3] calculations, should cause a high-field shift. C-1 is also flanked by two *sp*-hybridized carbon atoms which have been shown to give rise to a shielding effect at adjacent carbon atoms.[8] This effect, however, is not large enough to account for the strong shielding, as shown by the observation that the analogous atom, C^γ, in the cumulene (**3**), has a chemical shift of 119·3 p.p.m.,[9] > 130 p.p.m. to lower field. Moreover, the correlation between carbon-13 chemical shift and CNDO/2 calculated total charge densities observed for a series of cumulenes[9] can be extended to include C-1 of (**1**), so apparently (**1**), like keten, is experiencing very strong shielding arising from high electron density at C-1.

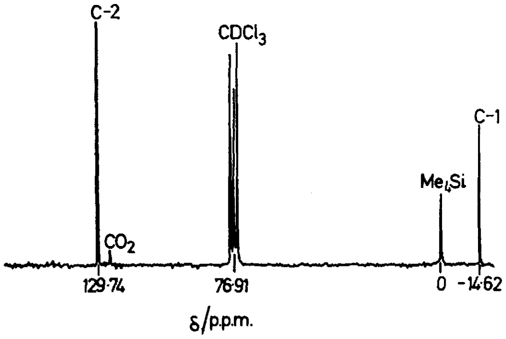


FIGURE. ^{13}C N.m.r. spectrum of C_3O_2 in $CDCl_3$ at −40 °C.

Unlike keten, however, the carbonyl chemical shift of (**1**) is at relatively high field (129·7 p.p.m.), close to that of carbon dioxide which appears as a small impurity in the spectrum. It is likely that at least part of this high field shift is due to the mutual shielding of the two adjacent *sp*-hybridized carbons in (**1**), which are not present in keten. A similar type of shielding effect was observed by Olah *et al.* in some studies on alkynoyl cations[10] where, upon formation of the cation, both the carbonyl and α-carbon atoms are substantially (*ca.* 20 p.p.m.) shielded relative to the precursors. The carbonyl carbon atom, in fact, has a chemical shift of 124·2 p.p.m. which is quite close to that of C-2 in (**1**). We feel that these ^{13}C data are consistent with considerable oxonium ion character at C-2, and a high electron density at C-1 as represented by resonance structure (**2**).

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[1] F. A. Miller, D. H. Lemmon, and R. E. Witokowski, *J. Phys. Chem.*, 1965, **21**, 1709.

[2] J. F. Olsen and L. Burnelle, *J. Phys. Chem.*, 1969, **73**, 2298.

[3] W. J. Hehre and J. A. Pople, *J. Amer. Chem. Soc.*, 1970, **92**, 2191; U. Gelius, C. J. Allan, D. A. Allison, H. Siegbahn, and K. Siegbahn, *Chem. Phys. Letters*, 1971, **11**, 224; J. R. Sabin and H. Kim, *J. Chem. Phys.*, 1972, **56**, 2195.

[4] L. A. Carreira, R. O. Carter, J. R. Durig, R. C. Lord, and C. C. Milionis *J. Chem. Phys.* 1973, **59**, 1028.

[5] J. B. Stothers, 'Carbon-13 NMR Spectroscopy,' Academic Press, New York, 1972.

[6] O. A. Gansow, A. R. Burke, and G. N. LaMar, *J.C.S. Chem. Comm.*, 1972, 456.

[7] J. Firl and W. Runge, *Angew. Chem.*, 1973, **85**, 671.

[8] G. A. Olah and P. W. Westerman, *J. Amer. Chem. Soc.*, 1973, **95**, 3706; G. L. Nelson, G. C. Levy, and J. D. Cargioli, *ibid.*, 1972, **94**, 3089.

[9] J. P. C. M. van Dongen, M. J. A. de Bie, and R. Steur, *Tetrahedron Letters*, 1973, 1371.

[10] G. A. Olah, R. J. Spear, P. W. Westerman, and J. M. Denis, *J. Amer. Chem. Soc.*, 1974, **96**, 5855.