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An INDO Investigation of the Electronic Structure and Hyperfine Coupling Constants of the Radicals HBO^-, HCO and HCN^-

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The equilibrium geometry and hyperfine coupling constants in the isoelectronic radicals HBO^-, HCO and HCN^- have been calculated using the INDO method. The calculated coupling constants are in reasonable agreement with experiment for these σ-radicals, provided the geometry is optimised in the calculations.

The E.S.R. spectra of the isoelectronic radicals HCO and HCN^- have been observed in the solid state and their hyperfine splitting constants measured [1–4]. Recently, the new isoelectronic radical HBO^- has been observed in γ-irradiated potassium borohydride and the observed splitting constants of this radical and those of the isoelectronic HCO and HCN^- have been discussed qualitatively by Symons and co-workers [5].

In view of a slight possibility [5] that the observed spectrum assigned to HBO^- was due to some other species, it is of interest to calculate the hyperfine coupling constants in these radicals using the semi-empirical all valence electron INDO method [6–8]. Symons *et al.* obtained the equilibrium bond angles from the $p:s$ ratio deduced from the observed anisotropic components of the hyperfine interaction tensors, and it is also of interest to see how this approximate method for calculating the angle compares with an INDO calculation in which the bond angle is determined by minimisation of the total energy. Previous work has shown that this method predicts equilibrium bond angles satisfactorily, and bond lengths rather less so [8]. HCO has previously been studied by Gordon and Pople and our results are in agreement with those reported in Ref. [8].

Energy minimisation was carried out for the radicals (HAB) by minimisation of the energy with respect first to the bond lengths HA and AB, followed by minimisation with respect to the HAB angle θ. Our results show very definitely that the calculated equilibrium bond angles are sensitive to the bond lengths, and the hyperfine coupling constants even more so.

The calculated minimum energy for HOB^- occurs at $\theta = 129°$ and $R(\text{B–O}) = 1.37$ Å, $R(\text{B–H}) = 1.25$ Å, whereas for HCN^-, the corresponding minimum occurs at $\theta = 133°$, $R(\text{C–N}) = 1.23$ Å and $R(\text{C–H}) = 1.18$ Å. The latter values are significantly greater than the values of $R(\text{C–N}) = 1.18$ Å, $R(\text{C–H}) = 1.09$ Å calculated for the neutral molecule [8]. For HCO, Gordon and Pople calculated $\theta = 131.2°$, $R(\text{C–H}) = 1.11$ Å, $R(\text{C–O}) = 1.22$ Å, whereas the experimental values are $\theta = 119.5°$, $R(\text{C–H}) = 1.11$ Å and $R(\text{C–O}) = 1.198$ Å [9]. In HCN^- and HBO^-

Table. *Valence electron charge density* q_i *s-electron spin density* ϱ_s, *and hyperfine coupling constants* a_i *in* HCO, HCN⁻ *and* HBO⁻ *at calculated equilibrium geometry*

Radical	atom	q_i	ϱ_s	a_i [a]	a_i^{exp} [a]
HCO	H	1.00	0.154	83.1	137
	C	3.85	0.173	141.6	135
	O	6.15	0.005	4.9	—
HCN⁻	H	1.25	0.292	157.6	137
	C	4.25	0.200	164.4	75.3
	N	5.50	0.006	2.4	6.5–7
HBO⁻	H	1.22	0.142	76.6	94
	B	3.32	0.284	—	100–101 [b] 33.5 [c]
	O	6.46	0.004	3.2	—

[a] Values in Gauss. [b] B^{11} nucleus. [c] B^{10} nucleus.

the calculated value of θ is close to the value deduced by Symons, although the errors in the experimental values are ~5°. In the case of HCO, INDO overestimates the angle, but the calculations probably give realistic values of the change in angle between these three radicals. The values of the valence electron charge densities at the calculated equilibrium geometry, the *s*-electron density and hyperfine coupling constants are given in the Table together with the experimental values. The boron splitting constant was not calculated due to the absence of sufficient data on boron compounds to calculate the scaling factor.

The calculated proton coupling constants are in quite good agreement with experiment and in particular the low value in HBO⁻ is correctly predicted. The value of $a_H = 74.9\,G$ for formyl calculated with $R(\text{C–H}) = 1.08$ Å, and $\theta = 120°$ [7] is much lower, however, than the observed value of 137 G, and compares with the values of $a_H = 83.0$ G for the calculated equilibrium geometry, and $a_H = 92$ G for the experimental geometry. The sensitivity of the results to the geometry are well illustrated by this example. The C^{13} coupling constant in HCN⁻ is about twice the observed value whereas a small value of a_N is predicted and observed in HCN⁻. It should be noted, however, that careful geometry optimisation is necessary for all these radicals since calculations using the standard bond lengths [8] for HCN⁻ predict an equilibrium angle of 125° and coupling constants $a_H = 86\,G$, $a(C^{13}) = 101$ G and $a_N = 5$ G, and although the N^{14} and C^{13} coupling constants are in better agreement with experiment, the proton coupling constant is much too low. One would expect that the bond lengths in ionic radicals should differ significantly from those in neutral molecules, and thus the use of standard bond lengths is an over simplification.

To summarise, the INDO method gives hyperfine coupling constants in reasonable agreement with experiment (except for C^{13} in HCN⁻) and predicts that these are all σ-radicals. The O^{17} splitting constant in HBO⁻ is predicted to be small (~3 G), and it will be interesting to see if this is in fact the case. The identity of the radical HBO⁻ thus seems to be confirmed by these calculations.

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