ab initio Molecular Orbital Investigations of Free Radicals. Part I. Structure and Reactivity of the ' Open-chain ' C_3H_3 Radical

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An *ab initio* MO approach has been used to study the structure of the open-chain radical C_3H_3. The results show that only one stable radical of this type exists, a π-delocalised propargylic structure. The reactivity of this radical has been examined on the basis of the calculated optimum geometry and of the spin density distribution.

MOLECULAR orbital theory has begun to be used extensively for the prediction of the equilibrium geometries of molecules.[1] At the level of *ab initio* quantum chemical calculations the results have been consistent with the experimental data, even when using a relatively poor basis set. The method has already been applied to molecules as large as substituted benzenes and has provided results of ' chemical ' interest.[2]

The possibility of computing optimum molecular bond lengths and angles is certainly very attractive for general applications, but it becomes of real interest in those cases where the determination of molecular geometry is experimentally very difficult or impossible.

Free radicals, for instance, are very often unstable or short-lived compounds whose geometry is in most cases impossible to determine by experimental means. On the other hand knowledge of the optimum geometry as well as of the charge and spin density distribution can be of significant help in understanding the chemistry of the species. For these reasons it seemed worthwhile to undertake an extensive *ab initio* investigation on various free radicals of chemical interest. The unrestricted Hartree–Fock treatment has been chosen on account of the need to obtain reliable spin density values;[3] and from a computational point of view, the Gaussian 70 series of programs[4] has been used.

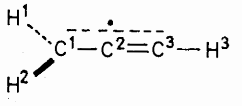
In the present paper we report results concerning the optimum structure, charge distribution, and spin densities of the ' open-chain ' C_3H_3 radical, together with some results concerning the dependence on the basis set of the computed spin densities and charge distribution.

RESULTS AND DISCUSSION

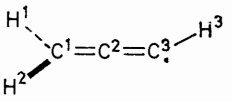
The present theoretical investigation aims to answer several questions which appear to be of critical importance for the understanding of the chemical behaviour of the open-chain C_3H_3 radical. This radical can be generated from acetylenic or allenic substrates [process (1)].

$$XCH_2C{\equiv}CH \xrightarrow{-X^\cdot} C_3H_3^\cdot \xleftarrow{-X^\cdot} CH_2{=}C{=}CHX \quad (1)$$

Chemical evidence shows that generation of C_3H_3 radicals from both acetylenic and allenic compounds gives a mixture of allenic and propargylic products in which the major component is in all cases the propargylic derivative.[5] These results have been rationalised by assuming for this radical the ambident, π-delocalised structure (Ia),[5] but the results could be as well explained by an equilibrium between the two species (Ia) and (Ib) (a localised σ radical-resembling allenic structure).



(Ia)



(Ib)

Therefore the first questions are how many stable open-chain C_3H_3 radicals can exist and what is the optimum geometrical structure of these species?

To this purpose we have computed the optimum geometry of the open-chain C_3H_3 radical at various fixed values of the out-of-plane angle α formed between the C(3)–H(3) bond and the plane containing the remaining atoms. The optimum geometry in each case is determined by optimising all the remaining parameters, except α, with the procedure described in ref. 6.

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[1] D. T. Clark, *Annual Reports B*, 1971, 43.

[2] W. J. Hehre, L. Radom, and J. A. Pople, *J. Amer. Chem. Soc.*, 1972, **94**, 1496.

[3] A. W. Salotto and L. Burnelle, *J. Chem. Phys.*, 1970, **53**, 333.

[4] W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, Quantum Chemistry Program Exchange, Indiana University.

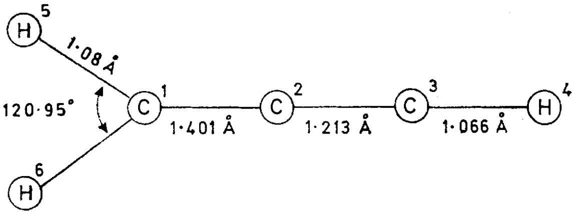
[5] R. M. Fantazier and M. L. Poutsma, *J. Amer. Chem. Soc.*, 1968, 5490 and references therein.

[6] M. D. Newton, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, 1970, **52**, 4064.

The final values of bond lengths and angles obtained in such a way are believed to be computationally accurate to <0·003 Å and 0·5° respectively.

The geometrical optimisation has been carried out at two different levels of accuracy, *i.e.* with a minimal basis set (STO-3G) [7] and with an extended one, 4–31G.[8a]

The values of the total energy and of the various geometrical parameters obtained with the two different basis sets are in good agreement, and show that only one stable paramagnetic species exists, whose optimum geometry, computed at 4–31G level, is shown in the Figure.



Computed optimum geometrical parameters for the open-chain C_3H_3 radical

The computed optimum value of the angle α is 0, the optimum value of the C(1)–C(2) distance is slightly greater than the average value of a double bond, while that of C(2)–C(3) is of the same order of magnitude as the value of a triple bond.

Therefore the present calculations show that the optimum structure of the C_3H_3 radical is of the π-delocalised propargylic type and that an ' allenyl ' free radical such as (Ib) does not exist since in the energy map investigated only one minimum has been found; even if the starting point of the optimisation of the geometrical parameters is assumed to be of allenic type, *i.e.* with both C–C bonds of 1·35 Å and H(3) out-of-plane by 60°, the resulting minimum is the ' propargylic ' radical (Ia). In chemical terms, this corresponds to an isomerisation of the incipient ' allenyl ' to ' propargyl ' radical without any activation energy barrier.*

It is noteworthy that a comparison based on the energy values of the two species (Ia and b) computed by the simple Hückel method produces the same conclusion.[9]

It must be pointed out that the present result refers to the gas phase where a molecule in isolation is considered. However this result is in agreement with the e.s.r. experimental data obtained by Kochi and Krusich.[10] These authors observed that the same paramagnetic species was produced by hydrogen abstraction from allene and propyne. Now, on the basis of the present investigation, it is possible to assign the geometry of the paramagnetic species experimentally observed.

The Table gives the atomic charges and spin densities of the radical species at the equilibrium geometry computed using three different levels of approximation. It can be seen that charges and spin densities differ significantly when computed at the minimal or at the extended level, while the difference is almost negligible between values obtained at the two extended levels.

Atomic charges (a),* total spin densities (b), and π-orbital spin densities (c) of the C_3H_3 radical at the equilibrium geometry, computed with various basis sets †

	a	b	c
		STO-3G	
C(1)	−0·109	+1·177	+0·857
C(2)	−0·039	−1·125	−0·461
C(3)	−0·108	+1·249	+0·604
H(4)	+0·106	−0·099	
H(5,6)	+0·076	−0·101	
		4-31G	
	a	b	c
C(1)	−0·193	+1·264	+0·848
C(2)	−0·146	−1·267	−0·450
C(3)	−0·350	+1·302	+0·602
H(4)	+0·315	−0·077	
H(5,6)	+0·187	−0·111	
		6-31G ‡	
C(1)	−0·197	+1·281	+0·851
C(2)	−0·129	−1·297	−0·451
C(3)	−0·393	+1·318	+0·600
H(4)	+0·347	−0·073	
H(5,6)	+0·186	−0·114	

* The value 0·00 corresponds to a neutral atom. † All values in atomic units. ‡ This basis set is described in ref. 8*b*.

These results seem to indicate that, in order to compute reliable values of the atomic charges and total spin densities of radicals, it is necessary to use extended basis sets. On the other hand, the π-orbital spin densities, whose importance to the chemical properties will be described later on, can be computed with a satisfactory accuracy with a minimal basis set. In order to assess the reliability of these values, it is worth testing how the computed spin densities compare with the experimentally measured quantities.

The parameters related to atomic spin densities are the isotropic hyperfine coupling constants, whose values can be derived from the e.s.r. spectrum. As is well known when the LCAO approximation is used, as in the present case, the isotropic hyperfine coupling constant of magnetic nucleus N, a_N, can be related to the spin density matrix $\rho^{\mathrm{spin}}_{\mu\nu}$ by means of equation (2) where

$$a_N = \frac{4\pi}{3} g\beta\gamma_N h\langle S_z\rangle^{-1} \sum_{\mu\nu} \rho^{\mathrm{spin}}_{\mu\nu}\, \phi_\mu(R)\phi_\nu(R) \qquad (2)$$

$\phi(R)$ denotes the value of the atomic orbital ϕ computed at the nuclear position of atom N, and the other symbols have the usual meaning (see for instance ref. 11).

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* Similar values for the geometrical parameters have been obtained with an INDO treatment (H. G. Benson, A. J. Bowles, A. Hudson, and R. A. Jackson, *Mol. Phys.*, 1971, **20**, 713).

[7] W. J. Hehre, R. F. Steward, and J. A. Pople, *J. Chem. Phys.*, 1969, **51**, 2657.

[8] (*a*) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, 1971, **54**, 724; (*b*) W. J. Hehre, R. Ditchfield, and J. A. Pople, *ibid.*, 1972, **56**, 2257.

[9] G. Giacometti, *Canad. J. Chem.*, 1959, **37**, 999.

[10] J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, 1970, **92**, 4110.

[11] J. A. Pople and D. L. Beveridge, ' Approximate Molecular Orbital Theory,' McGraw-Hill, New York, 1970.

No attempt has been made to calculate a_{N} according to equation (2). But, if we assume that contributions to the summation in (2) are negligible unless both ϕ_{μ} and ϕ_{ν} are centred on atom N, equation (2) becomes (3)

$$a_{\text{N}} = \left[\frac{4\pi}{3} g\beta\gamma_{\text{N}}h\langle S_z\rangle^{-1}|\phi_{s_{\text{N}}}(R)|^2\right]\rho^{\text{spin}}_{s_{\text{N}}s_{\text{N}}} \qquad (3)$$

where $\rho^{\text{spin}}_{s_{\text{N}}s_{\text{N}}}$ is the unpaired electronic population of the s orbitals of atom N and $|\phi_{s_{\text{N}}}(R)|^2$ is the density of the s orbitals of atom N evaluated at the nucleus, since only s functions have non-vanishing values at the nucleus and contribute to the isotropic hyperfine coupling constant.

Therefore the quantity in brackets can be assumed to be approximately constant for each type of magnetic nucleus and the ratio of hyperfine coupling constant of atoms of the same type should be of the same order of magnitude as the ratio of the corresponding computed spin densities.

In the propargyl radical a_{H_4} is 12·68 G and $a_{\text{H}5,6}$ is 18·92 G;[10] the corresponding ratio of 1·49 must be compared with the values 1·02, 1·44, and 1·56 obtained for the ratio $\rho s_{\text{H}_{5,6}} : s_{\text{H}_4}$ by using the spin density values computed with the STO-3G, 4–31G, and 6–31G basis sets, respectively. The value obtained by using the hyperfine coupling constants is very close to those computed by using the spin densities obtained at the extended levels, while the corresponding value at the minimal basis level is quite poor.

The result provides greater confidence in using the computed spin densities for discussing the chemical behaviour of the radical, since this satisfactory comparison between computed and measured quantities seems to suggest that at least the relative magnitude of the spin density values computed at the extended levels can be assumed to be correct.

As far as chemical behaviour is concerned the data in the Table indicate that the radical should have ambident character. Actually the experimental results show that in coupling and abstraction reactions, mixtures of acetylenic and allenic products are obtained with a predominance of acetylenic products, often in spite of their lower thermodynamic stability.[5] Thus, the reactivity of the radical seems not to be significantly affected by the thermodynamic stability of the products, and, when steric effects are negligible, an important factor in determining the orientation of attack on the radical is the relative magnitude of the spin densities at the two terminal carbon atoms. Total spin density values are approximately equal [1·28 and 1·32 at C(1) and C(3) respectively] and on this basis one would expect that products having acetylenic or allenic structure should be formed with roughly the same ease: this prediction is not in agreement with the experimental observations.

The experimental results can be explained by assuming that the important factor in determining the position of attack is the value of the orbital spin density in the direction of attack, in this case the π-orbital, and not the total spin density value, which is the sum of the various orbital spin densities. From the values in the Table it can be observed that the π-orbital spin density value at C(1) is significantly greater than the corresponding value at C(3). It seems intuitively correct for cases where a preferential direction of attack exists that the spin density value in this direction is an important determining factor.

Another factor which may significantly affect the reactivity of the radical is the charge distribution, which is in agreement with a π-delocalised propargylic structure. The maximum charge is at C(3) (—0·39), while C(1) is only slightly negative (—0·19) and C(3)–H(3) exhibits a polarisation of the acetylenic type.

At present results are not available from which it can be deduced whether charge density is more or less important than spin distribution in determining the reaction path of a homolytic reaction of an ambident radical with an electrophile or nucleophile. However research is in progress to gain information on this point.

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