A MINDO/3 and NDDO Study of Antiaromatic Three-membered Rings and their Valence Tautomers

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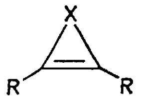
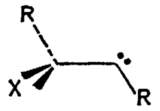
Summary Calculations using MINDO/3 and a newly parameterised version of NDDO indicate that antiaromatic heterocyclic analogues of the cyclopropenyl anion should be stable and may therefore occur as stable intermediates in reactions; calculations are also reported for the isomeric cyclic carbenes (hetero-analogues of cyclopropylidene) and for the isomeric acyclic carbenes (*e.g.* HCO–CH:), the acyclic carbenes being predicted to rearrange to the corresponding antiaromatic heterocycles without activation.

THERE has recently been much interest in the possible occurence of the antiaromatic heterocycles (I; X = O,[1] X = NR,[2] X = S[3]) as reaction intermediates and also in their energy relative to the isomeric carbenes (II), zwitterions (III), heterocumulenes (IV), and cyclic carbenes (V). We now report a study of the relative stabilities of these isomeric species using both the MINDO/3[4] method and a new semi-empirical method employing the NDDO approximation.[5] Calculated and observed heats of formation are shown in Table 1. The agreement between the values calculated by the two semi-empirical methods is generally good.

The antiaromatic heterocycles (I) were all calculated to lie in local energy minima, implying that if they are generated in chemical reactions they should form stable intermediates. The calculated structures of oxiren (Ia), 1*H*-azirine (Ib), and thiiren (Ic) are shown in the Figure. The olefinic sections of the heterocycles (I) were calculated to be essentially planar. In the case of oxiren (Ia) or thiiren (Ic) a second minimum of slightly higher energy (*ca.* 0·5 kJ mol⁻¹) was found corresponding to the *trans* distorted structure (VI), the torsional angle between the two CH bonds being *ca.* 60°.


(I)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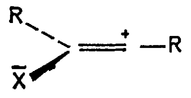
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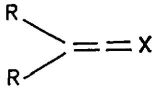
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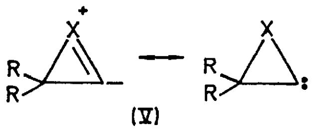
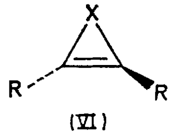
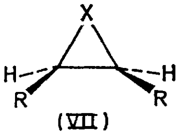

(V)


(VI)


(VII)

(a) $X = O$, $R = H$; (b) $X = NH$, $R = H$; (c) $X = S$, $R = H$; (d) $X = CH_2$, $R = H$; (e) $X = \bar{C}H$, $R = H$.

The carbenes (II) were found to be unstable, collapsing without activation to the heterocumulenes (IV). The same was true of the zwitterions (III). Both (II) and (III) were studied by fixing the HCC angle (=120°) in order to prevent rearrangement. Under these conditions two distinct minima were found in each case, one corresponding to (II) and the other to (III) with (II) the more stable. The zwitterions (III) can thus be regarded as the lowest singlet excited states of the carbenes (II).

TABLE 1. Calculated and Observed Heats of Formation

	Molecule	Heat of formation (kJ mol⁻¹) MINDO/3	NDDO	Obsd.
(Ia)	Oxiren	138·9	152·3	
(Ib)	1*H*-azirine	293·3	296·2	
(Ib)	*planar*	407·9	444·8	
(Ic)	Thiiren	205·4		
(Id)	Cyclopropene	248·5	261·9	278·7[6]
(Ie)	Cyclopropenyl anion	470·7	399·2	
(Ie)	*planar*	626·8	589·1	
(IIa)		215·1	238·5	
(IIIa)		240·6	298·3	
(IIb)		412·1	419·7	
(IIIb)		462·3	492·9	
(IIc)		320·5		
(IIIc)		324·3		
(Va)		75·7	84·9	
(Vb)		256·1	315·5	
(Vc)		284·1		

It is particularly significant that each carbene (II) was calculated to be considerably less stable (80—120 kJ mol⁻¹) than the corresponding heterocycle (I). This suggests that the heterocycles (I) may well be the products of reactions which have previously been regarded as giving the carbenes (II). A study of the ring opening of oxiren to keten [(Ia) → (IVa)], using MINDO/3, indicates that it occurs

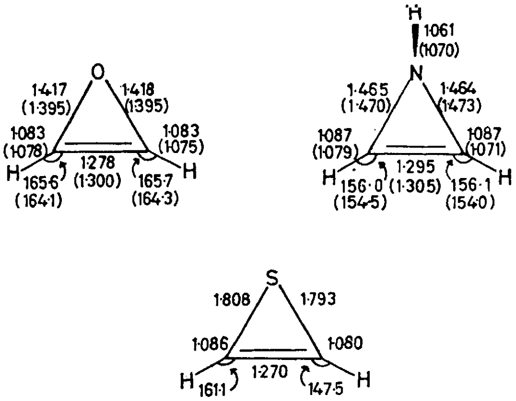


FIGURE. MINDO/3 (NDDO) structures for (a) oxiren (Ia); (b) 1*H*-azirine (Ib); (c) thiiren (Ic). Bond lengths in Å, bond angles in degrees. The small deviations from C_{2v} symmetry are probably due to incomplete convergence of the iterative (SIMPLEX) procedure used.

with an activation energy of *ca.* 80 kJ mol^{-1} with the carbene (IIa) lying very close to the transition state.

TABLE 2. Calculated and Observed Heats of Hydrogenation.[a]

	Molecule	Heat of Hydrogenation (kJ mol^{-1}) MINDO/3	NDDO	Obsd.
(Ia)	Oxiren	249·8	239·3	
(Ib)	1*H*-azirine	199·2	162·8	
(Ib)	*planar*	277·8	263·2	
(Ic)	Thiiren	207·5		
(Id)	Cyclopropene	212·6	225·5	225·5[6]
(Ie)	Cyclopropenyl anion	256·5	201·3	
(Ie)	*planar*	394·6	275·3	

[a] Calculated heats of hydrogenation correspond to the difference in the heats of formation of the molecules (I) and (VII) as calculated by MINDO/3 or NDDO.

Curious irregularities are seen in comparing the carbenes (V) with the isomeric heterocycles (I). Carbenes are usually less stable than the "normal" compounds found by rearrangement through 1,2-migration to the carbenoid centre [*e.g.* (V) → (I)]. Yet MINDO/3 and NDDO agree in predicting (Va) to be more stable than (Ia) by 60—70 kJ mol^{-1}. This difference could be attributed to destabilization of (I) by its antiaromaticity. If so one might expect (Ib) and (Ic) to be even more destabilized from analogy with the increase in aromaticity on passing from furan to thiophene or pyrrole. However, NDDO predicts (Ib) to be more stable than (Vb) by 19·3 kJ mol^{-1} and while MINDO/3 predicts (Vb) to be the more stable, the difference (37·2 kJ mol^{-1}) is less than for (Va) *vs.* (Ia). Moreover MINDO/3 predicts (Ic) to be much more stable than (Vc), the difference being 78·7 kJ mol^{-1}. It is difficult to account for these results in qualitative terms. We also studied the conversion of (Ia) into (Va), using MINDO/3; the calculated activation energy was 121 kJ mol^{-1}.

A measure of the antiaromatic destabilization of the unsaturated rings (I) can be obtained from their calculated heats of hydrogenation [(1) → VII)]. The change in ring strain for the reaction [(I) → (VII] should be about the same as for the hydrogenation of cyclopropene (I) into cyclopropane. The heats of hydrogenation of the heterocycles (I) relative to that of cyclopropene should therefore provide a measure of their antiaromaticity.

Calculated and observed heats of hydrogenation of (I) are shown in Table 2. For oxiren (Ia) the calculated heats of hydrogenation are in good agreement and are not substantially greater (*ca.* 25 kJ mol^{-1}) than the value for cyclopropene, suggesting that the antiaromatic destabilization of oxiren (Ia) is not large. This is not surprising since the aromatic energy of furan is small. For thiiren (Ic) the heat of hydrogenation is about the same for cyclopropene.

In the case of 1*H*-azirine (Ib) and the cyclopropenyl anion (Ie), the antiaromatic interactions are reduced by distortion from planarity at the nitrogen atom and the anionic carbon atom respectively.[7] A more realistic estimate of their antiaromaticity relative to oxiren (Ia) is provided by comparison with the planar species (Ib) and (Ic). From Table 2, the magnitude of the antiaromatic interactions in oxiren (Ia), planar 1*H*-azirine (Ib), and planar cyclopropenyl anion (Ie) increases as the electronegativity of the group X decreases, as would be expected on the basis of second-order perturbation theory.

Our results and conclusions, which lend support to reaction mechanisms involving the species (**I**) as intermediates, disagree with a recent study employing the extended Hückel method.[8] A full MINDO/3 study of the Wolff Rearrangement is in progress.

Recently, Hopkinson[9] reported *ab initio* calculations for some of the species discussed here. Since he did not optimize their geometries, his results are of uncertain significance. They do agree qualitatively with ours.

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