Three-membered Rings. Part I. Semiempirical Calculations of the Molecular Conformation of Compounds of the Type $\text{Ph}\overline{\text{CH}\cdot\text{X}\cdot\text{CH}}_2$ ($\text{X} = \text{CH}_2$, O, S, NH, or CCl_2)

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Semiempirical CNDO/2 calculations have been performed on the series of compounds phenylcyclopropane, phenyloxiran, phenylthiiran, phenylaziridine, and 1,1-dichloro-2-phenylcyclopropane. From the energies obtained, it is concluded that for all these molecules the most stable conformation is that in which the planes of the phenyl group and of the three-membered ring are orthogonal (or very close to orthogonal) to one another. These results indicate that inter-ring conjugation is present. The energy barrier to rotation about the phenyl–three-membered ring bond is $\leqslant 13.4$ kJ mol^{-1} for the first four compounds, which suggests that interconversion between one orthogonal form and another, equivalent to the first, is rapid at room temperature. Instead, 1,1-dichloro-2-phenylcyclopropane, because of the steric and electrostatic effects of the chlorine atoms, gives an energy barrier of 61.9 kJ mol^{-1}. For this reason interconversion in this molecule is slow.

INVESTIGATIONS of molecules containing three-membered rings adjacent to π-electron systems have clearly shown the presence of conjugative properties derived from the unsaturated character of these rings.[1-26] One of the classes of compounds which has been studied most extensively is the phenyl derivatives of such rings. However, although experimental data exist for the phenylcyclopropane series, there is much less information available on the phenyl derivatives of oxiran, thiiran, and aziridine. For all four series theoretical calculations are virtually non-existent.

In order to obtain information on the extent of conjugation between these rings and the phenyl group and on the preferred orientation of the latter with respect to the three-membered ring, studies are under way of their

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electric dipole moments,[27] charge transfer complexes,[28] and p.e. spectra [29] and these are backed up by MO calculations.

This paper describes the results of semiempirical CNDO/2 MO calculations, on the molecules $\mathrm{PhCH{\cdot}X{\cdot}CH_2}$, where X = $\mathrm{CH_2}$, O, S, NH, or $\mathrm{CCl_2}$. Of the dichloro-derivatives only that of phenylcyclopropane was investigated since the close similarity of the energy curves for X = $\mathrm{CH_2}$, O, S, and NH suggests that the conclusions drawn from the chlorocyclopropane derivative may be extended to the corresponding chloro-derivatives of the other three compounds.

RESULTS

The semiempirical method of Pople [30] was used for the calculations, which were performed on the Univac 1110 machine of Rome University, using a program supplied by the QCPE organization.[31] The parameters used were taken from ref. 32.

(a) *Molecules of the Type* $\mathrm{PhCH{-}X{-}CH_2}$ *with* X = $\mathrm{CH_2}$, O, S, *and* NH.—The geometrical data [33] used in the CNDO/2 calculations for these molecules are reported in Figure 1. Bond distances and angles were kept constant for all conformations. For phenylcyclopropane only the calculations were also performed using an angle γ of 55° 30′. These calculations have not been repeated for all the compounds examined because the variation in γ has little effect on the relative energies of the conformers and on the behaviour of the function $E = E(\phi)$ (see below). The energies for all the molecules were calculated by varying the angle ϕ between 0 and 180° at intervals of 30°. Figure 2 illustrates the energies obtained as a function of rotation angle ϕ. Energies reported are not absolute values but are referred to the minimum calculated value for each molecule. For the two phenylaziridine isomers the same zero value was assumed to allow comparison between the two sets of results.

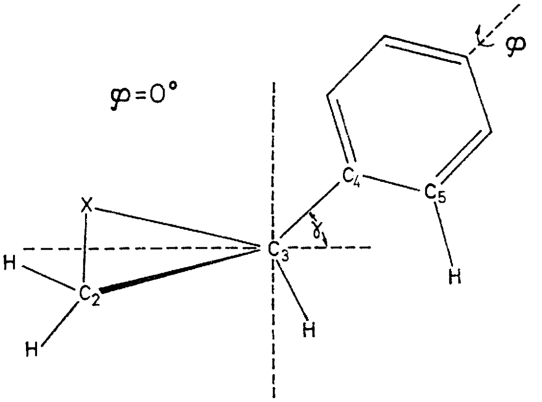
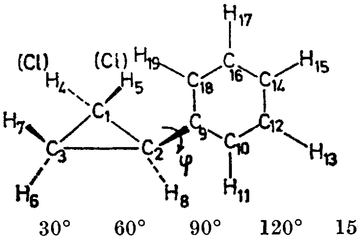


FIGURE 1 Geometrical parameters used in the CNDO/2 calculations for $\mathrm{PhCH{-}X{-}CH_2}$ molecules, where X is $\mathrm{C(1)H_2}$, O, S, NH, and $\mathrm{C(1)Cl_2}$. Bond lengths are in Å. Phenylcyclopropane, C(2)–C(3) 1.553, C(2)–H 1.105, C(3)–C(4) 1.505, C(4)–C(5) 1.08, C(5)–H 1.084, $\mathrm{C(1)\widehat{C}(2)C(3)}$ 60°, $\mathrm{H\widehat{C}(2)H}$ 114.6°, $\mathrm{C(4)\widehat{C}(5)H}$ 120°, γ 51.5°; phenyloxiran, C(2)–C(3) 1.47, C(2)–H 1.08, C(2)–O 1.44, $\mathrm{H\widehat{C}(2)H}$ 116.25°, $\mathrm{O\widehat{C}(2)C(3)}$ 59.3; phenylthiiran, C(2)–C(3) 1.492, C(2)–H 1.078, C(2)–S 1.819, $\mathrm{S\widehat{C}C(3)}$ 65.8°, $\mathrm{H\widehat{C}H(2)}$ 116°; phenylaziridine, C(2)–H 1.083, C(2)–N 1.488, N–H 1.00, angle between HC(2)–H plane and the C(2)–C(3) bond 159.4°, angle between CCN plane and the N–H bond 112°; 1,1-Dichloro-2-phenylcyclopropane: C–Cl 1.77 (unspecified parameters are equal to those for phenylcyclopropane)

Calculated charge densities



ϕ	0° *	30°	60°	90°	120°	150°	180°
Phenylcyclopropane							
C-1	4.010	4.017	4.018	4.015	4.010	4.007	4.010
C-2	3.932	3.983	3.984	3.985	3.984	3.983	3.982
C-3	4.010	4.007	4.010	4.015	4.018	4.017	4.010
H-4	0.996	0.995	0.997	0.999	0.999	0.998	0.996
H-5	0.997	0.998	0.999	0.999	0.998	0.997	0.997
H-6	0.997	0.998	0.999	0.999	0.998	0.998	0.997
H-7	0.996	0.998	0.999	0.999	0.997	0.995	0.996
H-8	1.101	1.008	1.003	1.000	1.003	1.008	1.101
C-9	3.954	3.955	3.958	3.960	3.958	3.955	3.954
C-10	4.014	4.013	4.001	4.007	4.010	4.014	4.015
H-11	1.009	1.009	1.009	1.008	1.006	1.007	1.008
C-12	3.983	3.984	3.986	3.987	3.886	3.984	3.983
H-13	1.010	1.010	1.009	1.009	1.009	1.010	1.010
C-14	4.005	4.004	4.000	3.998	4.000	4.004	4.005
H-15	1.009	1.009	1.009	1.009	1.009	1.009	1.009
C-16	3.983	3.984	3.986	3.987	3.986	3.984	3.983
H-17	1.010	1.010	1.009	1.009	1.009	1.010	1.010
C-18	4.015	4.014	4.009	4.007	4.008	4.013	4.014
H-19	1.008	1.007	1.007	1.008	1.009	1.009	1.009
1,1-Dichloro-2-phenylcyclopropane							
C-1	3.799	3.803	3.805	3.803	3.799	3.797	3.799
C-2	3.994	3.994	3.995	3.996	3.996	3.995	3.994
C-3	4.031	4.028	4.030	4.034	4.038	4.037	4.031
Cl-4	7.138	7.139	7.142	7.143	7.142	7.140	7.138
Cl-5	7.137	7.138	7.142	7.143	7.141	7.140	7.137
H-6	0.974	0.973	0.975	0.976	0.975	0.975	0.974
H-7	0.973	0.974	0.975	0.975	0.973	0.972	0.973
H-8	0.989	0.986	0.981	0.979	0.981	0.987	0.989
C-9	3.952	3.952	3.955	3.956	3.953	3.951	3.952
C-10	4.009	4.009	4.006	4.004	4.006	4.008	4.012
H-11	1.007	1.008	1.007	1.007	1.006	1.005	0.998
C-12	3.985	3.985	3.987	3.987	3.985	3.884	3.984
H-13	1.006	1.007	1.006	1.006	1.006	1.006	1.006
C-14	4.001	4.000	3.997	3.994	3.996	3.999	4.001
H-15	1.006	1.007	1.006	1.005	1.005	1.006	1.006
C-16	3.984	3.982	3.986	3.986	3.985	3.984	3.985
H-17	1.006	1.008	1.005	1.004	1.006	1.006	1.006
C-18	4.012	4.033	4.013	4.002	4.003	4.007	4.009
H-19	0.998	0.971	0.987	1.001	1.004	1.005	1.007

* ϕ = 0° when the two rings are perpendicular to one another.

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From Figure 2 it is seen that none of the four molecules has an energy minimum, not even a relative one, for $\phi = 90°$ or values close to this. Hence, the existence of forms of the perpendicular type (I) may be excluded. All four molecules show only a single minimum in the $E = E(\phi)$ function. This corresponds to $\phi = 0°$ for phenylcyclopropane, phenylthiiran, and an isomer of phenylaziridine (that with the hydrogen atom bonded to the nitrogen in the *cis*-position with respect to the phenyl group). Phenyloxiran and the other isomer of phenylaziridine give the preferred form at $\phi = 30°$. It may be concluded from these results that the most stable conformation is the bisected one (II), in which the C_2X and C_6 planes are orthogonal to one another. The fact that the angle ϕ is not the same for all four molecules is probably due to the different steric and electrostatic effects exerted by CH, O, S, and NH. The presence of the bisected isomer alone is in good agreement with both the experimental results [7,19,22–26] and with the few theoretical calculations performed to date, specifically, that for phenylcyclopropane.[23] The energies of both bisected and perpendicular forms were calculated for the phenylcyclopropane by the CNDO/2 method and it was found that the bisected form has a much lower energy than that

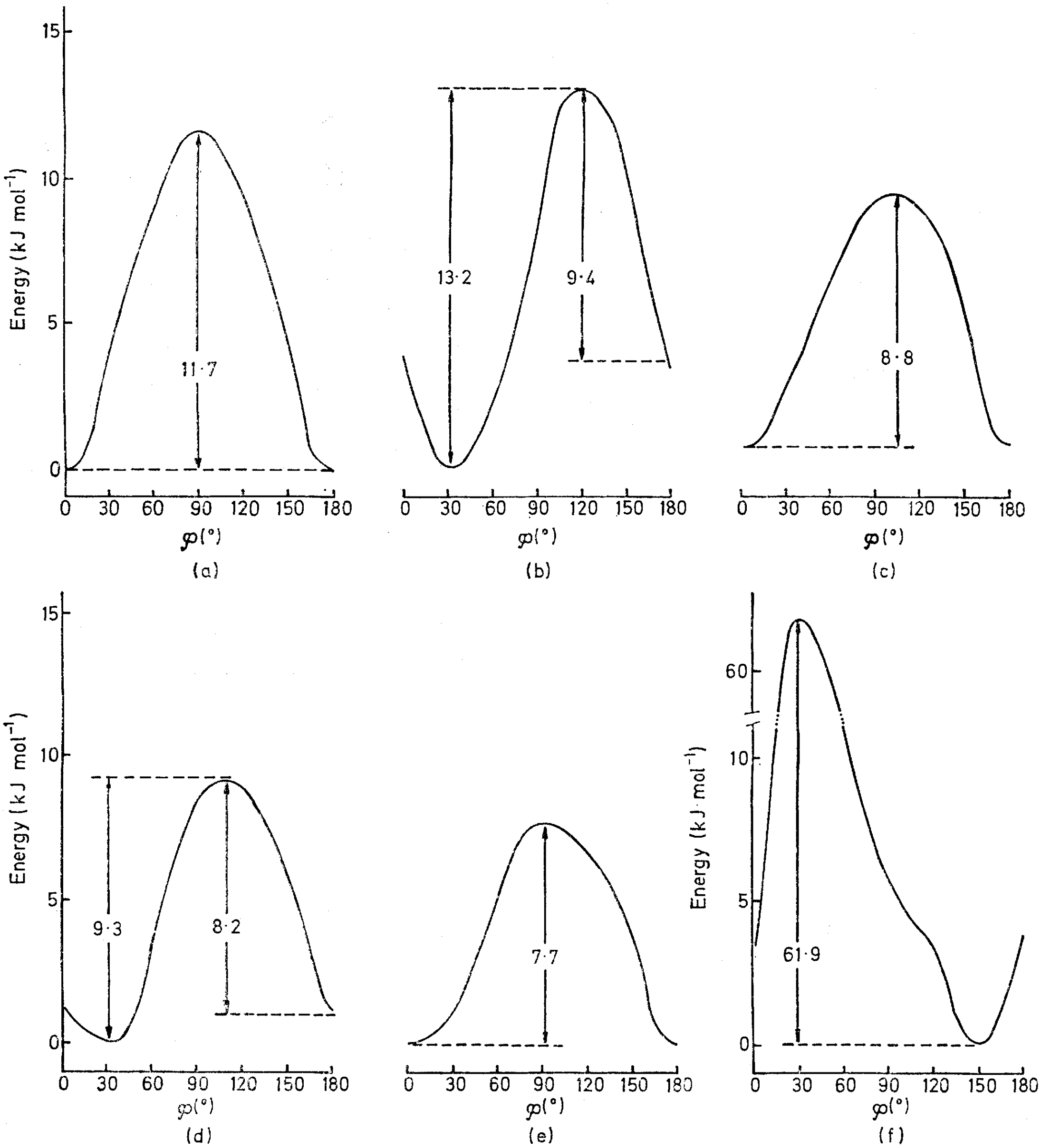
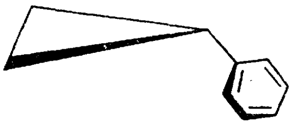
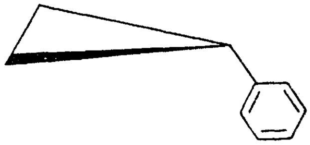


FIGURE 2 Energy curves for $\overline{\text{PhCH–X–CH}_2}$ molecules: (a) phenylcyclopropane; (b) phenyloxiran; (c) phenylthiiran; (d) and (e) phenylaziridine, the hydrogen bonded to nitrogen is, respectively, *cis* and *trans* relative to the phenyl ring; (f) 1,1-dichloro-2-phenylcyclopropane

of the perpendicular form (I) and is preferred. These theoretical results agree with recent measurements obtained in this laboratory on several charge transfer complexes between phenyl derivatives of oxiran (donor) and ICl (acceptor). The data obtained clearly indicate that there is an interaction between the electrons of the two rings. According to Walsh's model for cyclopropane,[34] this interaction is at maximum at $\phi = 0°$ (bisected conformer). However, it has been shown [35] that overlap between the suitable orbitals of cyclopropane with the adjacent system may still occur at angles of *ca.* 60° and hence inter-ring conjugation is possible.



(I)
$\phi = 90°$
Perpendicular



(II)
$\phi = 0°$
Bisected

Turning again to Figure 2, it may be noted that the difference between the energies of the bisected and perpendicular forms varies from 13.2 for phenyloxiran to 7.7 kJ mol^{-1} for phenylthiiran. These values also represent the height of the energy barrier to interconversion between the two equivalent bisected forms. This interconversion, brought about by rotation about the phenyl three-membered ring bond, is possible given the energies involved. Conversely, it is not possible to suggest the presence of a bisected–perpendicular equilibrium, although the energy difference between $\phi = 0$ and 90° would allow it.

Note that the difference between the energy of the bisected and perpendicular forms (ΔE) of phenylcyclopropane reported in ref. 23 is larger than that calculated here (44.5 compared with 11.7 kJ mol^{-1}). Because of this, as pointed out above, the calculations on this molecule were also repeated using an angle γ of 55° 30′, as well as one of 51° 30′. With this angle, a ΔE of 11.3 kJ mol^{-1} was obtained, compared with that of 11.7 kJ mol^{-1}, calculated using $\gamma = 51° 30'$.

Approximate calculations from n.m.r. spectra have been carried out for phenylcyclopropane.[25] Treating the molecule as a classical rotor and using a simple potential curve of the form $E_\alpha = E_0 + V/2(1-\cos 2\alpha)$, the value of ΔE was found to be of the order of 7.8 kJ mol^{-1}, which agrees with the value of 11.7 kJ mol^{-1}, calculated here.

The fact that the bisected form is favoured over the perpendicular one cannot be attributed to the presence of steric effects. In fact, the first is more hindered than the second. In order to obtain further clarification of this point, we have also investigated 1,1-dichloro-2-phenylcyclopropane for which there are experimental results.[22,24]

There is little essential difference between the $E = E(\phi)$ function and the energy barrier heights for rotation about the phenyl three-membered ring bond (8.8 and 9.3 kJ mol^{-1}, respectively) between the two isomers of phenylaziridine. Thus both isomers are equally stable.

(b) 1,1-*Dichloro-2-phenylcyclopropane*.—Calculations on this molecule were carried out using the same scheme as for phenylcyclopropane (Figure 1). The results of these calculations are illustrated in Figure 2 which indicates that, although the behaviour of the $E=E(\phi)$ function is similar to that in phenylcyclopropane, several important points of difference emerge. In fact, the function shows only a minimum at *ca.* 150 instead of 0° and a maximum at *ca.* 30 instead of 90°. The energy barrier to rotation about the phenyl–cyclopropane bond is much higher (61.9 compared with 11.7 kJ mol^{-1}) than in the unsubstituted analogue. This is clearly due to the presence of the two chlorine atoms, which may affect the barrier height in two ways, *via* the $-I$ inductive effect, which would favour delocalisation of the phenyl π electrons towards the cyclopropane ring, hence stabilising the bisected configuration even more and also *via* a steric and especially electrostatic effect on the hydrogen *ortho* to the phenyl group. Charge densities do not support the presence of the $-I$ inductive effect of the chlorine atoms (Table 1). This might be due to the $+M$ effect of the latter.

The above result seems reasonable since it shows that the effect of the *cis*-chlorine on the phenyl group is greater than that of hydrogen in the same position. Kerr constant measurements and electric dipole moment give differing results for the angle ϕ in 1,1-dichloro-2-phenylcyclopropane (120, 10,[22] and 150° [26]). The present results show that the preferred conformation is that with $\phi = 120$—150°, in agreement with steric requirements deduced from the diagrams obtained using the geometrical parameters of Figure 1 and van der Waals atomic radii.[36]

Conclusions.—The MO calculations reported here demonstrate that the preferred conformation of phenylcyclopropane, phenyloxiran, phenylthiiran, phenylaziridine, and 1,1-dichloro-2-phenylcyclopropane is the bisected one (or one very close to this, which is compatible with the steric and electrostatic effects exerted by X in $\mathrm{Ph\overline{CH{\cdot}X{\cdot}CH}_2}$). In the first four compounds the energy barrier to rotation about the phenyl three-membered ring bond allows rapid interconversion between the equivalent bisected forms. This situation appears to be present in benzene solution as found in the literature [22,26] and as

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deduced from the dipole moment of the derivative *m*-$ClC_6H_4\overline{CH-O-CH_2}$ (2.23 D), which indicates that free rotation about the phenyl three-membered ring bond is possible. In 1,1-dichloro-2-phenylcyclopropane, the steric and electrostatic effects exerted by the halogen do not allow the phenyl group to assume the same configuration as assumed in the unsubstituted compound and, because of the high energy barrier present, prevents rapid interconversion between the two bisected forms which are equivalent.

These results, which are in very good agreement with experimental data [7,19,22-24] and others from this laboratory,[27,28] are further supported by the following considerations. (i) All four non-halogenated derivatives give very similar $E = E(\phi)$ functions, despite the fact that structural parameters found by different authors, sometimes obtained using different techniques, were utilised. (ii) There is similarity between the calculated and observed moments: phenylcyclopropane μ_{obs} 0.49,[37] μ_{calc} 0.36 D; phenyloxiran μ_{obs} 1.83,[27] μ_{calc} 2.1 D; 1,1-dichloro-2-phenylcyclopropane μ_{obs} 1.91,[22] μ_{calc} 1.95 D.

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