INDO- and CNDO-Approximated Molecular Orbital Calculations on the Spin-Spin Coupling Constants in Some 2-Substituted Oxetanes

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Spin-spin coupling constants between the methine proton in the oxetane ring and the phenyl protons and carbon nuclei have been calculated in different conformations in the INDO approximation for 2-phenyloxetane and 2-(4-fluorophenyl)oxetane, and in the CNDO approximation for 2-(2-chlorophenyl)oxetane and 2-(3-chlorophenyl)oxetane. In each case the finite perturbation method has been used.

In the case of 2-(2-chlorophenyl)oxetane a fairly high energy barrier for the rotation around the C–C bond between the rings is obtained, while in the other three cases the barrier is much lower. The calculations predict an equilibrium conformation in which the oxygen atom lies almost in the plane of the aromatic ring.

The calculated dipole moments of 2-(2-chlorophenyl)oxetane and 2-(3-chlorophenyl)oxetane vary significantly with conformation.

1. Calculation Procedures and Estimation of Errors in *J*'s

All calculations were performed using the CNINDO (QCPE141) programme with the original parametrization, enlarged by three subprogrammes [1] for computing the spin-spin coupling constants.

According to the finite perturbation theory (FPT) [2], the spin-spin coupling constant between the nuclei N and N′ is, following the usual practice,

$$J_{\mathrm{NN'}} = \frac{\hbar}{2\pi}\left(\frac{8\pi\beta}{3}\right)^2 {}^2\gamma_{\mathrm{N}}\,\gamma_{\mathrm{N'}}\,s_{\mathrm{N}}{}^2(0)\,s_{\mathrm{N'}}{}^2(0)\;\frac{\varrho_{\mathrm{NN}}(p_{\mathrm{N'}})}{p_{\mathrm{N'}}} \tag{1}$$

when only the Fermi contact contribution is included. In Eq. (1), the γ's are the magnetogyric ratios for the nuclei N and N′, $\hbar$ is Planck's constant divided by 2π, β is the Bohr magneton, $s_{\mathrm{N}}{}^2(0)$ and $s_{\mathrm{N'}}{}^2(0)$ are the valence *s* orbital densities at the nuclei N and N′, ϱ_{NN} is the diagonal matrix element of the spin density matrix corresponding to the valence *s* orbital of atom N, and $p_{\mathrm{N'}}$ is the perturbation parameter. The perturbation was placed on the methine proton and $p_{\mathrm{N'}}$ was set to 10^{-3} hartree in each case.

In the original CNINDO programme the convergence is tested by the electronic energy, but in calculating the coupling constants the convergence criterion [3]

$$\left|\frac{\varrho_{\mathrm{NN}}^{\mathrm{old}} - \varrho_{\mathrm{NN}}^{\mathrm{new}}}{\varrho_{\mathrm{NN}}^{\mathrm{old}}}\right| \leqq 10^{-5} \tag{2}$$

was used. Since the coupling constant $J_{\mathrm{NN'}}$ is proportional to the matrix element ϱ_{NN} and the other factors are constants, an equation similar to (2) is obtained for $J_{\mathrm{NN'}}$;

$$\left|\frac{J_{\mathrm{NN'}}^{\mathrm{old}} - J_{\mathrm{NN'}}^{\mathrm{new}}}{J_{\mathrm{NN'}}^{\mathrm{old}}}\right| \leqq 10^{-5}\,. \tag{3}$$

Replacement of $|J_{\mathrm{NN'}}^{\mathrm{old}} - J_{\mathrm{NN'}}^{\mathrm{new}}|$ by $|\Delta J|$ gives for the change of the coupling constant

$$|\Delta J| \leqq 10^{-5}\,|J_{\mathrm{NN'}}^{\mathrm{old}}|\,. \tag{4}$$

Thus the change $|\Delta J|$ in the calculated coupling constant is equal to or less than $10^{-5}\,|J_{\mathrm{NN'}}^{\mathrm{calc}}|$ on the first iteration circle after convergence (2) has been reached. For example, if the calculated coupling constant is of the order of 1 Hz, the correction to this is $\leqq 10^{-5}$ Hz.

The maximum number of iterations was limited to 100 in the INDO calculations and to 50 in CNDO calculations. In the former ones the coupling constants converged after about 50–70 iterations in most conformations and always before 100. In the CNDO calculations, on the other hand, some *J*'s failed to converge.

The Cartesian atomic coordinates were calculated with the aid of the subroutine COORD [1] in each conformation. For the phenyl protons and carbons the coordinates of benzene were used [4]. The oxetane ring was approximated in 2-substituted oxetanes by a square with sides of 1.5 Å [5]. For the other bond lengths and bond angles the following data were applied [5]: $R(\mathrm{C}_\alpha - \mathrm{H}_\alpha) = 1.09$ Å. $R(\mathrm{C}_\beta - \mathrm{H}_\beta) = 1.10$ Å, $\sphericalangle\,\mathrm{H}_\alpha - \mathrm{C}_\alpha - \mathrm{H}_\alpha = 110^\circ\,18'$ and $\sphericalangle\,\mathrm{H}_\beta - \mathrm{C}_\beta - \mathrm{H}_\beta =$

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110° 44′. In normal oxetane $R(\mathrm{C-C})$ was 1.549 Å and $R(\mathrm{C-O})$ 1.449 Å, and the angles were $\sphericalangle \mathrm{C}_\alpha - \mathrm{C}_\beta - \mathrm{C}_\alpha = 84° 33'$ and $\sphericalangle \mathrm{C}_\alpha - \mathrm{O} - \mathrm{C}_\alpha = 91° 59'$. The alpha methylenes were assumed to lie in one plane perpendicular to the planar oxetane ring. For the C – F and C – Cl bond lengths, the typical values of 1.35 Å and 1.70 Å, respectively, were used, since no experimental results exist for the studied molecules. For the same reason the C – C bond between the rings was assumed to lie on the twofold axis of the phenyl ring and for its length the values 1.4 Å and 1.6 Å were used.

The coupling constants were calculated with different values of the rotational angle θ (see definition in Fig. 1), the intervals being 30° or 20°. The results were least squares fitted to the Karplus function [6]

$$J = a + b \cos \theta + c \cos 2\,\theta \qquad (5)$$

using the programme LINGR [7]. The same weights were given for all the data.

The computations were performed with UNIVAC 1108 and Honeywell 1644 computers.

2. H—H Coupling Constants

The main interest was directed to the long-range proton-proton coupling constants between the methine proton (proton 7) in the oxetane ring and the phenyl protons, because experimental results on these were available. The numbering of the atoms is illustrated in Figure 1.

The notations J^{o}, J^{m} and J^{p} usually refer to the coupling constants in benzene derivatives, but for the sake of convenience, they are here used for the coupling constants between the rings. For instance, J^{o} is the coupling constant between H7 and the protons H2 and/or H6, which are orto relative to the oxetane part.

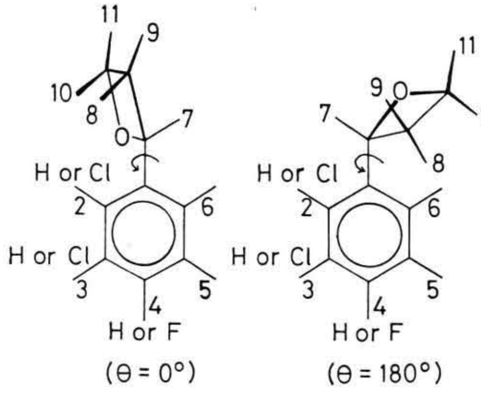

Fig. 1. Labelling of the nuclei and the definition of the rotational angle Θ.

2.1. 2-Phenyloxetane

The calculated long-range H – H7 coupling constants for 2-phenyloxetane have been listed in Table 1 and are presented graphically in Fig. 2 as a function of the angle θ. Fitting to Eq. (5) gives (in Herz)

$$\begin{aligned} J^{\mathrm{o}} &= -0.563 - 0.150 \cos \theta + 0.297 \cos 2\,\theta\,, \\ J^{\mathrm{m}} &= 0.477 + 0.352 \cos \theta - 0.094 \cos 2\,\theta\,, \\ J^{\mathrm{p}} &= -0.388 + 0.327 \cos 2\,\theta\,. \end{aligned} \qquad (6)$$

The behaviour of the coupling constants as functions of θ shows some interesting features, the ortho and para couplings having two maxima and minima when θ goes from 0° to 360°, the meta coupling only one. The maximum of J^{p} occurs when the partial dipole moment of the oxetane part lies perpendicular to the phenyl plane, i. e. $\theta = 0°$ or 180°, and the minimum when the oxetane moment is parallel to the phenyl plane, i. e. $\theta = 90°$ or 270°.

A comparison of the direct INDO results with the results obtained by the Eqs. (6) is given in Table 2. The value measured for J^{o} in $\mathrm{D_6}$-benzene solution is – 0.64 Hz [8]. The effect of the other two coupling

Table 1. Calculated H – H7 coupling constants of 2-phenyloxetane in different conformations at the INDO level of approximation.

Θ [a]	J^{o}_{67}	J^{o}_{27}	J^{m}_{57}	J^{m}_{37}	J^{p}_{47}	$J_{7,10}$	$J_{7,11}$
0	−0.411	−0.140	0.723	0.037	−0.062	−0.493	−0.350
30	−0.508	−0.218	0.773	0.082	−0.152	−0.482	−0.351
60	−0.795	−0.543	0.765	0.275	−0.483	−0.495	−0.362
90	−0.896	−0.832	0.628	0.501	−0.716	−0.515	−0.374
120	−0.692	−0.810	0.411	0.656	−0.620	−0.522	−0.382
150	−0.346	−0.574	0.171	0.713	−0.297	−0.515	−0.370
180	−0.140	−0.411	0.037	0.723	−0.062	−0.493	−0.350

[a] Rotational angle defined in Figure 1.

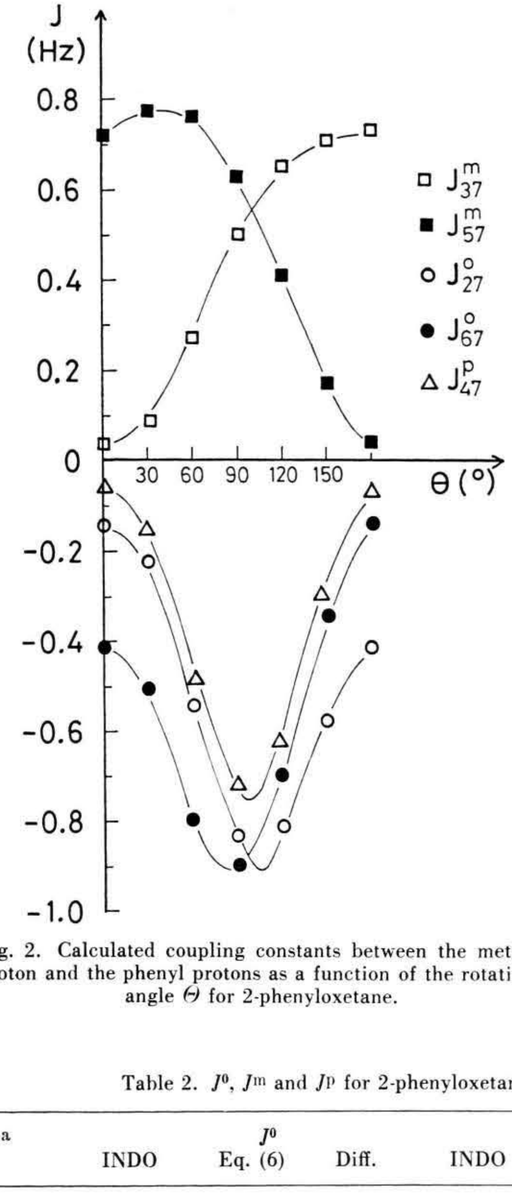

Fig. 2. Calculated coupling constants between the methine proton and the phenyl protons as a function of the rotational angle Θ for 2-phenyloxetane.

constants, J^m and J^p, could not be seen in the 300 MHz PMR spectra, the resolution of 0.4 to 0.6 Hz being too low. If free rotation around the C – C bond between the rings can be expected, the average values over the period 360° obtained from the Eqs. (6) are – 0.563 Hz, 0.477 Hz and – 0.388 Hz for J^o, J^m and J^p, respectively. Thus it seems that in this case the absolute value of the coupling constant decreases as the number of the bonds between the coupled protons increases. However, the minimum energy is obtained when θ is approximately 135°, corresponding to the conformation where the oxygen atom lies very close to the plane of the aromatic ring. Maximum energy is reached with $\theta = 60°$. The energy difference between these two conformations is about 4 kcal/mole. Still, the coupling constants which are obtained as the mean values of the two equivalent states with energy minima ($\theta = 135°$ and 315°) are very close to those in the case of free rotation.

In the previous work dealing with the 60 MHz PMR spectra of 2-(2,4-dichlorophenyl)oxetane and 2-(3,4-dichlorophenyl)oxetane, J^o and J^m were found to be opposite in sign [9]. The present calculations at the INDO level of approximation support this conclusion: they give J^o as negative, J^m as positive, and J^p again as negative in accordance with the Dirac vector model.

Zon et al. [10] were able also to resolve the long range "diagonal" coupling constants in the oxetane ring of 2-phenyloxetane. By comparing the observed and the calculated spectra and by performing tick-

Table 2. J^0, J^m and J^p for 2-phenyloxetane as calculated by INDO and by the Equations (6).

Θ [a]	J^0 INDO	J^0 Eq. (6)	J^0 Diff.	J^m INDO	J^m Eq. (6)	J^m Diff.	J^p INDO	J^p Eq. (6)	J^p Diff.
0	−0.411	−0.417	0.006	0.723	0.735	−0.012	−0.062	−0.013	−0.049
30	−0.508	−0.545	0.037	0.773	0.734	0.039	−0.152	−0.183	0.031
60	−0.795	−0.787	−0.008	0.765	0.700	0.065	−0.483	−0.528	0.045
90	−0.896	−0.860	−0.036	0.628	0.571	0.057	−0.716	−0.715	−0.001
120	−0.692	−0.637	−0.055	0.411	0.348	0.063	−0.620	−0.576	−0.044
150	−0.346	−0.285	−0.061	0.171	0.125	0.046	−0.297	−0.267	−0.030
180	−0.140	−0.117	−0.023	0.037	0.031	0.006	−0.062	−0.110	0.048
210	−0.218	−0.285	0.067	0.082	0.125	−0.043			
240	−0.543	−0.637	0.094	0.275	0.348	−0.073			
270	−0.832	−0.860	0.028	0.501	0.571	−0.070			
300	−0.810	−0.787	−0.023	0.656	0.700	−0.044			
330	−0.574	−0.545	−0.029	0.713	0.734	−0.021			
360	−0.411	−0.417	0.006	0.723	0.735	−0.012			

[a] Dihedral angle.

ling experiments, they could show that both couplings are negative, viz. -0.35 Hz (cis) and -0.26 Hz (trans). INDO calculations give about -0.36 Hz and -0.50 Hz, respectively. It seems that INDO overestimates the magnitudes of the trans H–H coupling constants in the above cases, although one must bear in mind that the oxetane ring may be puckered[11].

For unsubstituted oxetane (trimethylene oxide) the calculated diagonal coupling constants were -0.13 (cis) and $+0.23$ Hz (trans). The experimental values of Lozach and Braillon[12] are 0.20 Hz and 0.14 Hz, respectively.

2.2. 2-(4-fluorophenyl)oxetane

For 2-(4-fluorophenyl)oxetane, calculations were carried out with two different C–C bond lengths between the rings, namely with $R(\mathrm{C-C}) = 1.4$ Å and $R(\mathrm{C-C}) = 1.6$ Å. The results are given in Table 3. They can be reproduced to within approximately the same error limits as in Table 2 by the Eq. (7) in the former case (1.4 Å) and by the Eq. (8) in the latter (1.6 Å):

$$\begin{aligned} J^{\mathrm{o}} &= -1.233 - 0.204\cos\theta + 0.713\cos 2\theta\,, \\ J^{\mathrm{m}} &= 1.062 + 0.505\cos\theta - 0.228\cos 2\theta\,, \\ J^{\mathrm{p}}_{\mathrm{HF}} &= 1.291 - 0.956\cos 2\theta\,, \end{aligned} \tag{7}$$

and

$$\begin{aligned} J^{\mathrm{o}} &= -0.572 - 0.144\cos\theta + 0.310\cos 2\theta\,, \\ J^{\mathrm{m}} &= 0.478 + 0.332\cos\theta - 0.104\cos 2\theta\,, \\ J^{\mathrm{p}}_{\mathrm{HF}} &= 0.499 - 0.508\cos 2\theta\,. \end{aligned} \tag{8}$$

In the above equations, $J^{\mathrm{p}}_{\mathrm{HF}}$ is the coupling constant between the methine proton and the fluorine nucleus in the para position of the phenyl ring. As it is seen from Table 3 and the Eqs. (7) and (8), the magnitudes of the coupling constants are fairly sensitive to the C–C bond length between the rings. With the value 1.6 Å, however, the substituent effect of the fluorine atom is negligible [Eqs. (6) and (8)]. This is also true experimentally, since the analysis gave for J^{o} the value -0.63 Hz[13], which is within the error limits the same as in 2-phenyloxetane. Neither J^{m} nor $J^{\mathrm{p}}_{\mathrm{HF}}$ could be resolved in the spectrum of 2-(4-fluorophenyl)oxetane.

If free rotation could be imagined around the C–C bond, the average values calculated from Eqs. (8) would be -0.572 Hz for J^{o}, 0.478 Hz for J^{m} and 0.499 Hz for $J^{\mathrm{p}}_{\mathrm{HF}}$, while the Eqs. (7) would give approximately double these values. However, the situation is very much the same as in 2-phenyloxetane; there exists an energy barrier to the rotation. It is about 9.4 kcal/mole with $R(\mathrm{C-C}) = 1.4$ Å and 4.0 kcal/mole with $R(\mathrm{C-C}) = 1.6$ Å, and the most stable conformation is that where the

Table 3. H–H7 coupling constants of 2-(4-fluorophenyl)oxetane in different conformations at the INDO level approximation.

a) $R(\mathrm{C-C}) = 1.4$ Å

Θ *	J^{o}_{27}	J^{o}_{67}	J^{m}_{37}	J^{m}_{57}	$J^{\mathrm{p}}_{47} = J^{\mathrm{p}}_{\mathrm{HF}}$	$J_{7,10}$	$J_{7,11}$
0	−0.370	−0.713	0.342	1.314	0.498	−0.086	−0.125
30	−0.528	−0.894	0.431	1.435	0.296	−0.079	−0.137
60	−1.271	−1.641	0.796	1.517	1.487	−0.193	−0.174
90	−1.915	−1.995	1.192	1.364	2.376	−0.282	−0.185
120	−1.816	−1.616	1.381	1.029	2.021	−0.220	−0.262
150	−1.192	−0.853	1.374	0.592	0.907	−0.122	−0.230
180	−0.713	−0.370	1.314	0.342	0.498	−0.086	−0.125

b) $R(\mathrm{C-C}) = 1.6$ Å

Θ *	J^{o}_{27}	J^{o}_{67}	J^{m}_{37}	J^{m}_{57}	$J^{\mathrm{p}}_{47} = J^{\mathrm{p}}_{\mathrm{HF}}$	$J_{7,10}$	$J_{7,11}$
0	−0.141	−0.400	0.048	0.693	−0.003	−0.490	−0.350
30	−0.219	−0.498	0.094	0.750	0.108	−0.480	−0.351
60	−0.555	−0.802	0.290	0.756	0.620	−0.493	−0.360
90	−0.854	−0.919	0.517	0.633	1.019	−0.511	−0.371
120	−0.828	−0.717	0.658	0.426	0.875	−0.517	−0.379
150	−0.516	−0.359	0.695	0.185	0.368	−0.510	−0.369
180	−0.400	−0.141	0.693	0.048	−0.003	−0.490	−0.350

* As defined in Figure 1.

Table 4. H—H7 coupling constants of 2-(2-chlorophenyl)oxetane in different conformations in the CNDO approximation with $R(\mathrm{C-C})=1.4$ Å.

Θ	J^{o}_{67}	J^{m}_{37}	J^{m}_{57}	J^{p}_{47}	$J_{7,10}$	$J_{7,11}$
0 [1]	−0.04	0.22	0.82	−0.01	−0.24	0.03
30	−0.06	0.20	0.80	−0.02	−0.23	0.03
60	−0.03	0.05	0.45	−0.02	−0.31	−0.01
90 [1]	0.04	0.01	0.08	−0.01	−0.38	−0.04
120	0.10	0.23	−0.00	−0.00	−0.35	−0.10
150	0.13	0.58	0.11	−0.01	−0.32	−0.02
180	0.08	0.84	0.25	−0.02	−0.28	0.10
210	0.10	0.74	0.21	−0.01	−0.28	0.06
240 [1]	0.12	0.40	0.05	−0.02	−0.26	−0.16
270 [1]	0.06	0.09	0.01	−0.01	−0.34	−0.08
300	0.04	0.00	0.24	−0.01	−0.33	−0.11
330	−0.01	0.10	0.59	−0.01	−0.24	−0.06
360 [1]	−0.04	0.22	0.82	−0.01	−0.24	0.03

[1] Coupling constants did not converge.

Table 5. H—H7 coupling constants of 2-(3-chlorophenyl)oxetane in different conformations in the CNDO approximation with $R(\mathrm{C-C})=1.4$ Å.

Θ	J^{o}_{27}	J^{o}_{67}	J^{m}_{57}	J^{p}_{47}	$J_{7,10}$	$J_{7,11}$
0	0.08	−0.03	0.84	−0.02	−0.24	0.02
20	0.08	−0.04	0.85	−0.03	−0.23	0.03
40	0.09	−0.07	0.72	−0.03	−0.24	0.03
60	0.08	−0.03	0.46	−0.01	−0.30	−0.01
80	0.06	0.02	0.18	−0.01	−0.36	−0.01
100	0.05	0.05	0.02	−0.01	−0.36	−0.05
120	0.04	0.09	−0.00	−0.02	−0.33	−0.09
150	−0.01	0.12	0.11	−0.04	−0.27	−0.06
180 [1]	−0.05	0.08	0.23	−0.06	−0.24	0.02
210	−0.08	0.08	0.21	−0.06	−0.23	0.02
240	−0.04	0.08	0.05	−0.03	−0.30	−0.01
270 [1]	0.04	0.05	0.01	−0.01	−0.36	−0.03
300	0.10	0.04	0.24	−0.00	−0.33	−0.09
330	0.12	−0.00	0.60	−0.01	−0.27	−0.06
360	0.08	−0.03	0.84	−0.02	−0.24	0.02

[1] Not all J's converged.

Table 6. C—H7 coupling constants of 2-phenyloxetane in different conformations calculated at the INDO level of approximation with $R(\mathrm{C-C})=1.6$ Å.

Θ	$J_{\mathrm{C2\text{-}H7}}$	$J_{\mathrm{C6\text{-}H7}}$	$J_{\mathrm{C3\text{-}H7}}$	$J_{\mathrm{C5\text{-}H7}}$	$J_{\mathrm{C4\text{-}H7}}$	$J_{\mathrm{C1\text{-}H7}}$	$J_{\mathrm{C4\text{-}H7}}$
0	2.631	5.113	−0.372	0.423	0.185	−2.075	123.96
30	2.687	4.662	−0.632	0.068	0.484	−2.402	124.78
60	2.597	3.934	−1.552	−1.083	1.599	−3.190	124.27
90	2.787	3.251	−2.107	−1.949	2.388	−3.616	122.63
120	3.517	2.657	−4.597	−1.848	2.067	−3.298	122.59
150	4.450	2.556	−0.405	−1.008	0.976	−2.545	123.34
180	5.113	2.631	0.423	−0.372	0.185	−2.075	123.96

Table 7. C—H7 coupling constants of 2-(4-fluorophenyl)oxetane in different conformations at the INDO level of approximation with $R(\mathrm{C-C})=1.4$ Å and $R(\mathrm{C-C})=1.6$ Å.

a) $R(\mathrm{C-C})=1.4$ Å

Θ	$J_{\mathrm{C2\text{-}H7}}$	$J_{\mathrm{C6\text{-}H7}}$	$J_{\mathrm{C3\text{-}H7}}$	$J_{\mathrm{C5\text{-}H7}}$	$J_{\mathrm{C4H\text{-}7}}$	$J_{\mathrm{C1\text{-}H7}}$	$J_{\mathrm{C7H\text{-}7}}$
0	6.262	10.677	−0.501	0.500	0.438	−4.440	124.51
30	6.478	9.866	−1.032	−0.180	1.053	−4.994	125.83
60	6.268	8.625	−3.255	−2.655	3.639	−6.540	125.61
90	6.473	7.369	−4.784	−4.526	5.533	−7.477	123.44
120	7.690	6.179	−3.867	−4.156	4.829	−6.898	123.21
150	9.355	6.033	−1.347	−2.084	2.317	−5.409	123.93
180	10.677	6.262	0.500	−0.501	0.438	−4.440	124.51

b) $R(\mathrm{C-C})=1.6$ Å

Θ	$J_{\mathrm{C2\text{-}H7}}$	$J_{\mathrm{C6\text{-}H7}}$	$J_{\mathrm{C3\text{-}H7}}$	$J_{\mathrm{C5\text{-}H7}}$	$J_{\mathrm{C4\text{-}H7}}$	$J_{\mathrm{C1\text{-}H7}}$	$J_{\mathrm{C4\text{-}H7}}$
0	2.625	5.243	−0.393	0.428	0.191	−2.031	124.34
30	2.676	4.758	−0.666	0.054	0.509	−2.349	125.21
60	2.590	4.010	−1.610	−1.122	1.643	−3.189	124.81
90	2.807	3.308	−2.193	−2.108	2.463	−3.661	123.24
120	3.585	2.682	−1.669	−1.223	2.138	−3.344	123.14
150	4.558	2.561	−0.430	−1.053	1.009	−2.543	123.77
180	5.243	2.625	0.428	−0.393	0.191	−2.031	124.34

rotational angle θ is about 135°, in other words when the oxygen atom of the oxetane ring is approximately in the plane of the phenyl ring. For this conformation J^0_{calc} is also in reasonable agreement with J^0_{exp}.

2.3. *2-(2-Chlorophenyl)oxetane and 2-(3-chlorophenyl)oxetane*

CNDO approximation does not estimate the long-range H – H7 coupling constants between the rings as well as does INDO. Even when the C – C bond length was taken to be 1.4 Å, some of the couplings were of a different order of magnitude compared with those calculated by INDO or observed.

The 100 MHz PMR spectra of the phenyl protons of 2-(2-chlorophenyl)oxetane and 2-(3-chlorophenyl)oxetane have recently been analysed [14]. In 2-(2-chlorophenyl)oxetane J^{o} was -0.88 Hz, the meta-couplings $J_{37}{}^{m}$ and $J_{57}{}^{m}$ were 0.49 Hz and 0.12 Hz, respectively, and J^{p} was -0.63 Hz whereas in 2-(3-chlorophenyl)oxetane $J_{27}{}^{o} = -0.76$ Hz, $J_{67}{}^{o} = -0.68$ Hz, $J^{m} = 0.37$ Hz and $J^{p} = -0.36$ Hz. The error limits are somewhat greater for the latter substance, since the spectrum (AA′BC part of the AA′BCX spin system) of the phenyl protons is not very sensitive to individual coupling constants, but rather to the sums of some coupling constants.

The calculated values are given in the Tables 4 and 5. As in 2-phenyloxetane and 2-(4-fluorophenyl)oxetane, the total energy of 2-(3-chlorophenyl)-oxetane has its minimum when the rotational angle θ is about 135°. The energy difference between the ground state and the most unstable state ($\theta = 60°$) is about 10 kcal/mole [$R(\text{C}-\text{C}) = 1.4$ Å]. The calculation of the total energy of 2-(2-chlorophenyl)-oxetane leads to two clear maxima at $\theta = 60°$ and $\theta = 240°$ and one minimum at $\theta = 135°$. The great second maximum ($\theta = 240°$) seems to arise from the repulsion between the chlorine atom and the oxygen atom. The energy difference between the states $\theta = 135°$ and $\theta = 240°$ is about 78 kcal/mole with $R(\text{C}-\text{C}) = 1.4$ Å.

Table 8. C–H7 coupling constants of 2-(2-chlorophenyl)oxetane in different conformations at the CNDO level of approximation with $R(\text{C}-\text{C}) = 1.4$ Å.

Θ	$J_{\text{C2-H7}}$	$J_{\text{C6-H7}}$	$J_{\text{C3-H7}}$	$J_{\text{C5-H7}}$	$J_{\text{C4-H7}}$	$J_{\text{C1-H7}}$	$J_{\text{C7-H7}}$
0	4.92	6.86	0.09	0.60	0.02	−0.88	102.97
30	4.44	5.56	0.05	0.49	0.03	−0.78	103.17
60	1.70	2.40	−0.02	0.28	0.03	−0.04	101.69
90 *	−0.07	0.21	0.02	0.10	0.01	0.60	99.37
120	1.47	0.41	0.23	0.00	0.01	0.39	99.08
150	5.01	2.66	0.47	0.03	0.01	−0.25	100.25
180	7.48	4.56	0.52	0.10	0.02	−0.65	101.05
210	6.70	4.12	0.62	0.06	0.01	−0.68	100.46
240 *	2.94	1.60	0.44	−0.01	0.01	0.02	99.86
270 *	0.20	−0.05	0.08	0.03	0.02	0.70	99.62
300	0.52	1.31	−0.01	0.22	0.02	0.39	100.54
330	2.91	4.48	0.03	0.46	0.02	−0.35	102.14
360 *	4.92	6.86	0.09	0.60	0.02	−0.88	102.97

* Not all J's converged.

Table 9. C–H7 coupling constants of 2-(3-chlorophenyl)oxetane in different conformations at the CNDO level of approximation with $R(\text{C}-\text{C}) = 1.4$ Å.

Θ	$J_{\text{C2-H7}}$	$J_{\text{C6-H7}}$	$J_{\text{C3-H7}}$	$J_{\text{C5-H7}}$	$J_{\text{C7-H7}}$	$J_{\text{C1-H7}}$	$J_{\text{C7-H7}}$
0	4.79	7.17	0.11	0.57	0.02	−0.92	101.16
20	4.82	6.70	0.10	0.52	0.03	−0.93	101.55
40	3.63	4.66	0.05	0.39	0.04	−0.58	101.65
60	1.68	2.50	−0.01	0.27	0.03	−0.02	100.73
80	0.18	0.80	−0.01	0.16	0.02	0.48	99.36
100	0.09	−0.06	0.09	0.05	0.01	0.65	98.90
120	1.44	0.42	0.27	−0.00	0.02	0.45	99.54
150	4.92	2.78	0.59	0.02	0.03	−0.23	100.83
180 *	7.52	4.69	0.77	0.07	0.03	−0.73	101.50
210	6.08	4.28	0.63	0.05	0.04	−0.59	102.03
240	0.27	1.67	0.37	−0.01	0.03	0.11	100.98
270 *	0.25	−0.06	0.13	0.03	0.02	0.65	99.05
300	0.41	1.35	−0.00	0.21	0.02	0.37	99.43
330	2.82	4.68	0.04	0.44	0.02	−0.39	100.58
360	4.79	7.17	0.11	0.57	0.02	−0.94	101.16

* Not all J's converged.

3. C—H Coupling Constants

The calculated C – H7 coupling constants between the methine proton H7 and the carbon nuclei in the phenyl ring are listed in the Tables 6 – 9 for the 2-substituted oxetanes. The J_{CH} values over one bond in the oxetane ring are also given. However, there are no corresponding experimental values in the literature, except for J^{α}_{CH} and J^{β}_{CH} in trimethylene oxide: $J^{\alpha}_{\mathrm{CH}} = 148.0$ Hz and $J^{\beta}_{\mathrm{CH}} = 137.3$ Hz [15]. INDO gives 135.56 Hz and 129.84 Hz, respectively. The calculated values for J^{α}_{CH} $(= J_{\mathrm{C7-H7}})$ in 2-phenyloxetane and 2-(4-fluorophenyl)oxetane are lower by about 10 Hz if compared with the values in oxetane, while J^{α}_{CH} is greater by about 0.5 Hz in 2-(4-fluorophenyl)oxetane than in 2-phenyloxetane. The other C – H7 coupling constants seem to be independent of the 4-substituent in the phenyl ring. The CNDO approximation gives about 100 Hz for J_{CH} in both chloro-substituted phenyloxetanes and a mean value greater by about 0.5 Hz in 2-(2-chlorophenyl)oxetane than in 2-(3-chlorophenyl)oxetane. The other C – H7 constants do not deviate very much from each other in these two molecules.

4. Dipole Moments

The dipole moments for some oxetane derivatives have recently been measured in solutions [16]. In normal oxetane μ is found to be 1.88 D (calculated 2.03 D), in 2-phenyloxetane 1.87 D (2.28 D), and in 2-(4-fluorophenyl)oxetane 2.51 D [calculated with $R(\mathrm{C-C}) = 1.4$ Å 2.75 D and with $R(\mathrm{C-C}) = 1.6$ Å 2.84 D]. Other 2-substituted oxetanes have also been studied, but not 2-(2-chlorophenyl)oxetane and 2-(3-chlorophenyl)oxetane. In Fig. 3 the calculated dipole moments of these two molecules are illustrated in different conformations. In both cases μ depends a lot on conformation (see Fig. 3); in 2-(2-chlorophenyl)oxetane it goes up from about 0.33 D $(\theta = 270^{\circ})$ to about 4.23 D $(\theta = 120^{\circ})$, and in 2-(3-chlorophenyl)oxetane from about 1.57 D $(\theta = 270^{\circ})$ to about 4.34 D $(\theta = 100^{\circ})$.

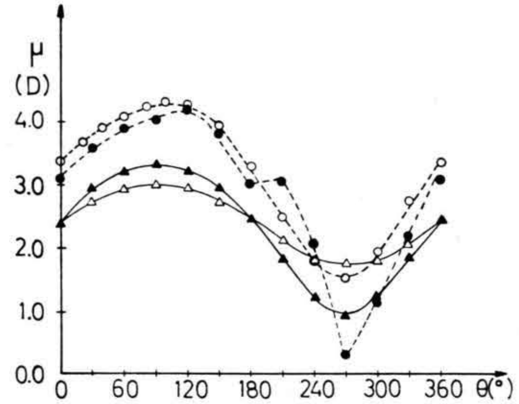

Fig. 3. Calculated electric dipole moments (in Debyes) versus rotational angle in 2-(2-chlorophenyl)oxetane and 2-(3-chlorophenyl)oxetane. Black circles and triangles are the dipole moments obtained by CNDO and vector calculation for 2-(2-chlorophenyl)oxetane and the open ones are the corresponding values for 2-(3-chlorophenyl)oxetane.

Figure 3 also shows the corresponding dipole moments obtained by simple vector addition of the main partial moments, i.e. dipole moments of oxetane and chlorobenzene.

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