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All Valence-Electron Calculations on *trans*-1-Phenyl-1-propene and its Anion Radical

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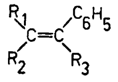
A series of all valence-electron calculations has been performed for different molecular conformations of *trans*-1-phenyl-1-propene. The various bond lengths and bond angles were kept constant except for the torsional angle between the plane containing the side chain and the plane of the ring. For the neutral molecule the CNDO/2 calculations suggest a nonplanar conformation to be the most stable, the equilibrium torsional angle being 30°. The EHT calculations give unrealistic results. INDO calculations for the anion radical suggest the planar conformation to be the most stable. The hydrogen coupling constants for different torsional angles are also given and the coupling constants after annihilation of the quartet state contaminant are discussed in relation to the experimental results.

Electron resonance data strongly suggest that in anion radicals of compounds with the general formula I, such as 1-phenyl-1-propene,[1] stilbene,[2] and styrene,[3] all the aromatic protons are magnetically inequivalent. In complicated molecules, where deuteration cannot be used as a tool for the assignment of the experimental coupling constants to protons in definite positions of the molecule, the assignment can be made, at least tentatively, by the comparison of experimental data with coupling constants obtained by molecular orbital calculations.



I

In π-electron calculations of Hückel type, the observed inequivalency of the coupling constants cannot be reproduced, because the geometry of the molecule is not explicitly used and all the overlap integrals between non-neighbours are neglected. Nevertheless HMO calculations have been tried, with variation of either the Coulomb integral[4] ("α-effect") or the resonance integral [4,5] ("β-effect") to account for the observed inequivalency. The former model implies a repulsion, the latter an imaginary bond between one *ortho*-proton and one ethylenic β-proton. These two empirical approaches have been used with reasonable success in a number of cases.[2,4–8]

Theoretically such calculations are less satisfactory. In addition to the original HMO parametrization and the McLachlan λ, they involve one more parameter, the value of which is chosen to give the best agreement with experiment. One would rather like to have a method with fewer adjustable parameters and which treats directly the core polarization effects leading to the hyperfine interaction. The SCF-MO theory with Intermediate Neglect of Differential Overlap, INDO [9,10] fulfills this requirement. This approximation deals with all the valence electrons on the same basis, and can therefore handle also "σ-radicals" or radicals with σ- and π-fragments within the same framework. Thorough discussions of this and related approximations are given in several texts.[11–17] In addition, in the *trans*-1-phenyl-1-propene molecule the possibility of a nonplanar equilibrium conformation has to be taken into account. Thus this molecule represents a rather complicated dynamic problem. The side chain as a whole performs torsional oscillations about the equilibrium position. The authors therefore found it a further matter of interest to examine the form of the potential function required to describe the torsional oscillations of the side chain in the neutral molecule and in its anion radical. For this purpose MO calculations have been performed for conformations with different angles of torsion around the C_1-C_7 bond (Fig. 1) using the EHT (Extended Hückel Theory) and the CNDO/2 method (Complete Neglect of Differential Overlap, version 2) for the neutral molecule, and the INDO method for the anion radical. Furthermore the methyl group in the side chain is a slightly hindered rotator. Experimentally it has been shown, however, that the methyl proton splittings are equivalent,[1] indicating that these protons are interconverting rapidly compared with the electron resonance time scale.

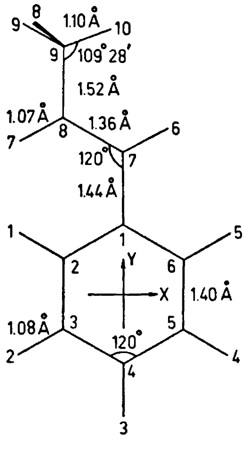


Fig. 1. Bond lengths (Å) and bond angles in *trans*-1-phenyl-1-propene.

PARAMETRIZATION

The Extended Hückel method has been outlined by Hoffmann.[18] The exchange integrals were calculated in terms of the diagonal elements and overlap integrals according to the Wolfsberg – Helmholz formula[19] ($K = 1.75$).[18] The overlap integrals were calculated from Slater orbitals with the usual orbital exponents (1.200 for hydrogen [20] and 1.625 for carbon [21]).

The CNDO/2 and INDO methods have been described by Pople and coworkers.[9–11,22–25] The atomic parameters for these calculations were taken from Ref. 11, pp. 75 – 83.

As no experimental geometry for the *trans*-1-phenyl-1-propene appears to be available, an idealized geometry has been built up for the molecule using fragments from similar molecules.[26–28] The bond lengths and bond angles used are shown in Fig. 1. The programs used in the calculations were all based on programs distributed by the QCPE organisation.[29] The EHT calculations were performed on an IBM 360/50 computer at the State Computer Center in Helsinki using a double precision version of Hoffmann's program,[30] written by L. Backström at the University Computing Center. The CNDO/2 and INDO calculations were carried through on a Burroughs 6500 computer at the Computing Center of the University of Helsinki, using slightly modified versions of the QCPE programs number 91 and 141, written by G. A. Segal and P. A. Dobosh, respectively.[31]

RESULTS AND DISCUSSION

The equilibrium position of the propene side chain. The torsional angle in *trans*-1-phenyl-1-propene and its anion radical is defined as the angle between the plane of the aromatic ring and the plane which contains the methyl group carbon atom and the ethylenic double bond. The electronic energies for different angles of torsion in the neutral molecule were obtained in the EHT calculations. The CNDO/2 calculations for the neutral molecule give the total energies for different torsional angles. Plots of the electronic and the total energy, respectively, *versus* the angle of torsion are shown in Figs. 2 and 3.

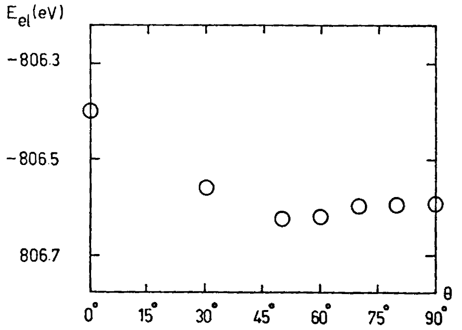


Fig. 2. The total electronic energy of *trans*-1-phenyl-1-propene as a function of torsional angle between the aromatic ring and the plane containing the side chain (EHT).

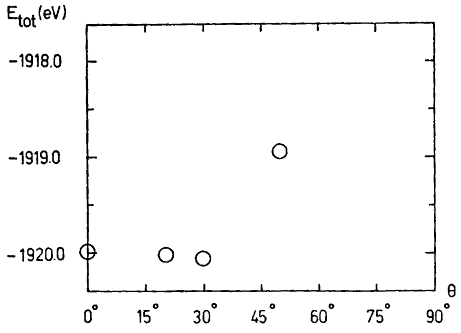


Fig. 3. The total energy of *trans*-1-phenyl-1-propene as a function of torsional angle between the plane of the ring and the plane containing the side chain (CNDO/2).

A nonplanar equilibrium conformation is suggested in both cases. In the EHT calculations the minimum energy for the molecule occurs for a conformation with an angle of torsion of about 50°C. The CNDO/2 calculations suggest a minimum of total energy for a conformation with an angle of torsion of about 30°.* However, the differences between the results obtained from these two approximations are more significant in other respects. The EHT calculations suggest that the planar conformation is less stable than the conformation with a torsional angle of 90° (energy difference 0.233 eV = 22.5 kJ/mol). The CNDO/2 calculations give lower energy for the planar form than for the conformations with torsional angles larger than 30°. The energy difference in this case between the planar and the 30° conformations is 0.097 eV = 9.36 kJ/mol. With increasing angle of torsion the energy increases rapidly, and is 1.13 eV = 109.0 kJ/mol higher for the conformation with a torsional angle of 50° compared with the 30° conformation. No definitive experimentally established geometry seems to exist for *trans*-1-phenyl-1-propene. Suzuki, basing his arguments on the position of the A band in the UV spectrum of substituted styrenes, concluded that the most probable conformation of styrenes with no substituents at hindering positions, is planar or nearly planar in solution.[32]

It is a well established fact that the molecular conformation in radical ions[33] and in excited states[34] may differ significantly from the stable conformation for neutral molecules in the ground state. It is therefore not surprising that the INDO calculations performed for the anion radical of *trans*-1-phenyl-1-propene suggest the minimum of total energy for the planar con-

Table 1. Calculated net charges for *trans*-1-phenyl-1-propene with different torsional angles between the aromatic ring and the plane containing the side chain.

Atom	Net charges (CNDO/2) 0°	20°	30°	50°
C_1	0.041	0.042	0.042	0.039
C_2	−0.014	−0.013	−0.013	−0.014
C_3	0.010	0.010	0.011	0.015
C_4	−0.001	−0.001	−0.002	0.000
C_5	0.010	0.011	0.011	0.015
C_6	−0.013	−0.013	−0.014	−0.016
C_7	−0.018	−0.017	−0.016	−0.015
C_8	−0.001	−0.003	−0.004	−0.006
C_9	−0.011	−0.010	−0.009	−0.007
H_1	−0.004	−0.005	−0.005	−0.005
H_2	−0.007	−0.007	−0.007	−0.006
H_3	−0.007	−0.007	−0.007	−0.007
H_4	−0.007	−0.007	−0.007	−0.007
H_5	−0.006	−0.006	−0.006	−0.006
H_6	0.000	0.002	0.004	0.008
H_7	0.012	0.010	0.008	0.006
H_8	0.007	0.006	0.005	0.003
H_9	0.007	0.008	0.006	0.006
H_{10}	0.012	0.003	0.002	0.002

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* *Note added in proof*: Recently Beringhelli *et al.*[46] obtained a torsional angle of 12° using a different semi-empirical approach and a theoretically optimized geometry.

formation. A plot of the total energy *versus* the angle of torsion is shown in Fig. 4. In addition to the prediction of different equilibrium conformations for the neutral molecule and the anion radical, it is seen that the potential energy for the torsional motion is much steeper for the neutral molecule. For the radical the energy difference between the planar and the 50° conformation is only 0.413 eV = 39.8 kJ/mol.

Net charges, dipole moments and bond indices. The net charges for the neutral *trans*-1-phenyl-1-propene obtained in the CNDO/2 calculations with different torsional angles are shown in Table 1. The corresponding values for the anion radical of this parent compound obtained in the INDO calculations are listed in Table 2. The variations in net charge with torsional angle are not large but systematic. With increasing torsional angle the charge difference between the side chain and the aromatic ring decreases in the neutral molecule as well as in the anion radical. This is reflected as a decrease in the calculated

Table 2. Calculated net charges for the anion radical of *trans*-1-phenyl-1-propene with different torsional angles between the aromatic ring and the plane containing the side chain.

Atom	Net charges (INDO) 0°	20°	30°	50°
C_1	−0.010	−0.014	−0.019	−0.046
C_2	−0.062	−0.058	−0.054	−0.043
C_3	0.028	0.026	0.024	0.016
C_4	−0.103	−0.103	−0.104	−0.112
C_5	0.022	0.022	0.022	0.022
C_6	−0.059	−0.059	−0.058	−0.055
C_7	−0.054	−0.050	−0.044	−0.012
C_8	−0.178	−0.176	−0.173	−0.162
C_9	0.107	0.106	0.106	0.103
H_1	−0.051	−0.054	−0.056	−0.065
H_2	−0.077	−0.077	−0.077	−0.078
H_3	−0.073	−0.073	−0.073	−0.075
H_4	−0.078	−0.078	−0.078	−0.080
H_5	−0.066	−0.067	−0.067	−0.070
H_6	−0.072	−0.072	−0.072	−0.078
H_7	−0.038	−0.039	−0.043	−0.042
H_8	−0.087	−0.087	−0.086	−0.083
H_9	−0.087	−0.086	−0.088	−0.083
H_{10}	−0.062	−0.062	−0.061	−0.058

Table 3. Calculated dipole moments for *trans*-1-phenyl-1-propene with different torsional angles between the aromatic ring and the plane containing the side chain (CNDO/2).

Torsional angle	Dipole moment (D)
0°	0.33
20°	0.30
30°	0.25
50°	0.16

dipole moments with increasing angle of torsion. The dipole moments obtained are listed in Table 3. Obviously the decrease in dipole moments with increasing torsional angle is due to the fact that the conjugation between the aromatic ring and the side chain decreases as the torsional angle increases.

The localized bond indices for the neutral molecule in the CNDO/2 approximation and for its anion radical in the INDO approximation were calculated according to Wiberg.[35] The major draw-back of this method is that antibonding interactions are lost in the squaring procedure. Another method of calculating bond indices has recently been introduced by Ehrenson and Seltzer,[36] and the Mulliken population analysis [37] in the CNDO and INDO approximations has been discussed by Kaufman.[38] The calculated bond indices for the *trans*-1-phenyl-1-propene molecule and its anion radical vary systematically as expected with the degree of conjugation between the aromatic ring and the side chain. The variations in the bond indices mean that the equilibrium geometry of the molecule varies continuously as the side chain performs torsional oscillations around its equilibrium position. In fact it has been shown [39–41] that in more accurate calculations of molecular properties, especially torsional barriers, one has to use a flexible geometry for the molecule. In the present case minimization with respect to at least the following parameters should be performed: the C_1-C_7 bond length, the $C_2C_1C_7$ and $C_1C_7C_8$ bond angles, and the torsional angle. The variations in the C_1-C_2, C_1-C_6, and C_7-C_8 bond lengths and the $C_1C_2H_1$, $C_1C_6H_5$, and $C_7C_8H_7$ bond angles are probably of less significance. However, the authors decided to use the nonflexible model partly because the approximations inherent in the CNDO and INDO methods make accurate calculations impossible, and partly because the flexible model would have required much more computer time.

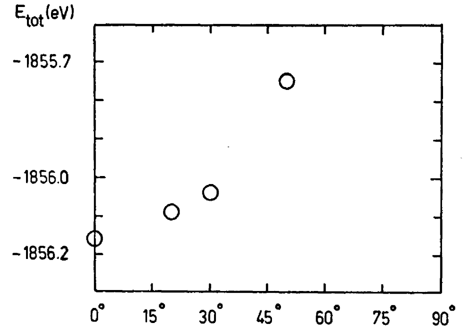

Fig. 4. The total energy of the anion radical of *trans*-1-phenyl-1-propene as a function of torsional angle between the aromatic ring and the plane containing the side chain (INDO).

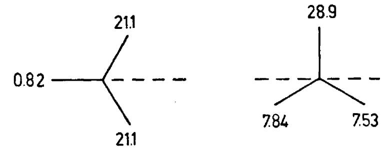

Fig. 5. The two orientations of the methyl group used in the calculation of the methyl hydrogen coupling constants. The indicated coupling constants are those obtained from the INDO calculations without annihilation.

The hyperfine coupling constants for the anion radical. The hydrogen hyperfine coupling constants were calculated according to the formulas:[11 42]

$$a_{\mathrm{H}} = 539.86\ \varrho_{s\mathrm{H}s\mathrm{H}} \qquad \text{(without annihilation)}$$
$$a_{\mathrm{H}} = 711.25\ \varrho_{s\mathrm{H}s\mathrm{H}} \qquad \text{(with annihilation)}$$

where $\varrho_{s\mathrm{H}s\mathrm{H}}$, the diagonal elements of the spin density matrix, indicate the unpaired electronic population of the s-orbital of the hydrogen atom under consideration. The hydrogen coupling constants obtained for the anion radical of *trans*-1-phenyl-1-propene are listed in Table 4. The coupling constants are found to vary considerably with the torsional angle. An interesting feature is that the coupling constant for the proton H_6 changes sign and increases, while the coupling constant for the proton H_7 decreases with increasing torsional angle.

Table 4. Calculated hydrogen coupling constants for the anion radical of *trans*-1-phenyl-1-propene with different torsional angles between the aromatic ring and the plane containing the side chain (INDO without annihilation).

	Coupling constants			
Hydrogen	0°	20°	30°	50°
1	−3.84	−3.68	−3.47	−2.93
2	1.85	1.78	1.68	1.28
3	−5.45	−5.50	−5.56	−6.03
4	1.48	1.54	1.60	1.71
5	−3.13	−3.19	−3.24	−3.37
6	−0.92	0.92	3.34	12.0
7	−9.34	−9.04	−8.79	−7.49
8	21.1	19.6	18.2	14.2
9	21.1	21.7	22.3	19.5
10	0.82	0.80	0.77	0.63

The methyl group hydrogen hyperfine coupling constants were calculated for two fixed orientations of this group with respect to the plane containing the ethylenic double bond and the aromatic ring (planar conformation). These orientations are indicated in Fig. 5, where also the corresponding splitting constants are shown. As the methyl group rotates through 360° around the C_8-C_9 bond the coupling constant for a particular hydrogen atom varied between 0.82 and 28.9 G. If one assumes entirely free rotation for the methyl group, the effective splitting constant may be calculated as an arithmetic average. This treatment indicates a methyl group hydrogen hyperfine splitting constant of the order of magnitude of 15 G. After annihilation of the quartet state contaminant,[42] the hyperfine splitting constants shown in Fig. 6a are obtained. The experimental splitting constants,[1] and the calculated coupling constants before annihilation also for the planar conformation are shown in Figs. 6b and 6c, respectively. In contrast to earlier findings for other molecules [42] it is seen that the annihilation procedure in this case reduces the calculated coupling constants to about one half their original value. For the methyl group hydrogens, the calculated coupling constant even after annihilation is as high as 12.7 G, which is about three times the one found experimentally,

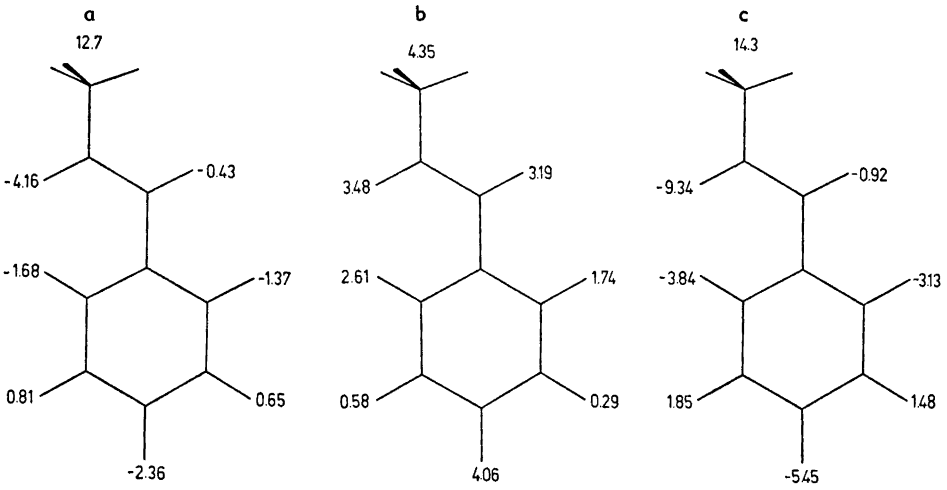

Fig. 6. The hydrogen coupling constants of the anion radical of *trans*-1-phenyl-1-propene. a. Calculated, INDO with annihilation. b. Experimental. c. Calculated, INDO without annihilation.

4.35 G. Obviously this would lead to an electron resonance spectrum with an over all width of at least 30 G. The width of the experimental spectrum was, however, found to be only 23.25 G. This is a serious discrepancy between theory and experiment, especially keeping in mind that good agreement between experiment and theory has been found for, *e.g.*, styrene using the unrestricted Hartree Fock method.[43] The authors wish to point out one possible explanation for this discrepancy. Free rotation was assumed for the methyl group around the C_8-C_9 bond. This is only approximately true. Assuming that the methyl group may be treated as a rigid top bonded to a rigid framework, the potential energy of the reorientation about the threefold symmetry axis of the top may be expressed by the modified Fourier series [41,44]

$$V(\alpha) = \frac{V_3}{2}(1- \cos 3\alpha) + \frac{V_6}{2}(1- \cos 6\alpha) + \ldots$$

where V_3 is the height of the threefold potential barrier and so on. In most cases V_6 and higher terms may be neglected. α is the angular coordinate which describes the torsional motion of the top. Substitution of this potential function into the Schrödinger equation leads to the Mathieu equation. The eigenvalues of the Mathieu equation which are lower than V_3 correspond to torsional oscillations, whose eigenfunctions can be approximated with the harmonic oscillator eigenfunctions. For eigenfunctions greater than V_3, the torsional oscillations go over into simple rotation, and the eigenfunctions of this motion can be approximated with the aid of the eigenfunctions for a rigid plane rotator.[45] For higher values of the torsional quantum number the probability distribution for the oscillator resembles that of the classical oscillator. Then one might say that the methyl protons spend a longer time in the plane defined by the ethylenic double bond, where the calculated splitting has a minimum (0.82 G), than in the plane perpendicular to this plane, where the calculated splitting reaches its maximum (25.4 G annihilated). This would lead to a splitting lower than the arithmetic mean value used. The calculations also give a tenfold splitting for H_7 with respect to H_6, whereas they were assumed to be of the same order of magnitude in the assignment of the experimental spectrum.[1] For the theoretical model this difference is reduced by the torsional oscillations around the equilibrium conformation (Table 4).

Since it is impossible to assign the coupling constants to the proper positions in the molecule without the aid of spectra of deuterated compounds, the possibility that the calculations give the right succession must be taken into account. The simulated spectrum using the coupling constants given in Ref. 1 is also considerably broader than the spectrum obtained experimentally. Although some of the small peaks in the wings of the spectrum may be hidden in the background noise, it seems us that the set of coupling constants given in Table 5 better reproduced the experimental spectrum. Selectively deuterated products of *cis*- and *trans*-1-phenyl-1-propene are in preparation. We therefore hope to return to the problem with the assignment of the coupling constants.

Table 5. Tentative experimental coupling constants of the anion radical of *trans*-1-phenyl-1-propene.

Coupling constant (G)	Number of hyperfine components
4.35	4
4.06	2
2.61	2
1.74	2
1.16	2
0.87	2
0.58	2
0.29	2

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