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An SCF-CI Study of Steric Effects in Hydrocarbon Molecules Containing Phenyl or Naphtyl Groups, in Relation with their Electronic Spectra

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SCF-CI study of the conformation of hydrocarbon molecules containing a phenyl or a naphtyl group: Prediction is made of the angle of twist between the plane of the phenyl or naphtyl group and the plane of the other part of the molecule, from ultraviolet absorption spectra recorded in the liquid phase.

Aus SCF-Rechnungen einerseits und gemessenen UV-Spektren andererseits wurden Rückschlüsse auf den Winkel, um den eine Phenyl- bzw. Naphthylgruppe aus der Ebene der restlichen Moleküls gedreht ist, gezogen.

Etude par la méthode SCF-CI de la géométrie de certains hydrocarbures contenant un groupe phényle ou naphtyle. L'examen des spectres d'absorption ultraviolets en phase liquide permet d'évaluer l'angle des deux plans contenant respectivement le groupe phénylê ou naphtyle et le reste de la molécule.

Introduction

The interaction of π electrons is maximal when a π system is planar. It will be reduced if, for any reason, the system deviates from the planar geometry. The electronic spectrum will, of course, be affected by this change in the geometry of the system. Accurate calculations of this spectrum may therefore often permit to determine the true non planar conformation of the molecule.

Numerous such studies have been made of the angle of twist in the biphenyl molecule [1, 4, 5, 6, 7, 8, 11, 12, 21, 22, 24]. This angle was determined to be 0° in the crystalline state, 18°—23° in the liquid phase and 42° in vapour phase, in good agreement with experimental values.

The hydrocarbon molecules investigated in this paper are: 1-phenylnaphthalene, 2-phenylnaphthalene, 9,10-diphenylanthracene, 1,2'-dinaphtyl and 2,2'-dinaphtyl, all in the liquid phase. We attempted to estimate the value of the angle of twist in each case.

Method and Parameters

We used the SCF-MO-CI formalism of the Pariser-Parr-Pople method [16, 17, 18] with the variable β approximation of Nishimoto and Forster [13, 14]. The configuration interaction process included the five highest occupied orbitals and the five lowest empty ones. The two center electronic repulsion integrals between non-neighbouring atoms were computed from a geometry, where all molecules were assigned regular polygonal structures with equal atom-atom bond lengths (1.4 Å) along the rings and all bond angles set equal to 120°. The twisted bond was assumed to be of constant length 1.5 Å as in the case of crystalline biphenyl [23] for all values of the angle of twist θ.

The two-center core integrals, the bond lengths (except the twisted bond that was kept equal to 1.5 Å) and the two-center repulsion integrals between neighbouring atoms were adjusted at every iteration by means of the relations:

$$\begin{aligned}
\beta_{\mu\nu} &= -0.51\, p_{\mu\nu} - 2.04 && \text{for the phenyl groups}\\
\beta_{\mu\nu} &= -0.51\, p_{\mu\nu} - 1.90 && \text{for the naphtyl groups}\\
\beta_{\mu\nu} &= -0.51\, p_{\mu\nu} - 1.84 && \text{for the anthracene part}\\
r_{\mu\nu} &= -0.18\, p_{\mu\nu} + 1.517 && \text{in all cases}\\
\gamma_{\mu\nu} &= \frac{14.397}{a_{\mu\nu} + r_{\mu\nu}} && [15]
\end{aligned}$$

The semiempirical parameters used were:

$$I_C = 11.16\ \text{eV} \quad \text{and} \quad \gamma_C = 11.13\ \text{eV}.$$

In the determination of the β value for the twisted bond, use was made of the approximate proportionality of β and the $\pi - \pi$ overlap integral S [9]. Thus, the value of β for the benzene ring bonds was reduced by the factor: $S_{1.4}/S_{1.5} = 0.859$ [10].

For $\theta = 0°$: $\beta_{\text{twisted}} = -2.39 \times 0.859 = -2.05$ eV.

For $\theta > 0°$, we admitted the validity of the relation: $\beta_{\text{twisted}} = -2.05 \times \cos\theta$ [22].

Results

The computed and experimental electronic singlet transition energies and oscillator strengths of the absorption spectra in the liquid phase of the five hydrocarbons studied are summarized in Figs. 1–5.

The experimental values of the oscillator strengths f were estimated from the absorption curves by means of the usual relation:

$$f = 4.32 \times 10^{-9} \times \varepsilon_{\max} \times \Delta\bar{\nu} \qquad [20]$$

where $\Delta\bar{\nu}$ is the band width (in cm^{-1}) at half-maximum extinction.

It may be seen from Figs. 1 and 2 that in the cases of 1,2′-dinaphtyl and 2,2′-dinaphtyl the computed spectrum for $\theta = 0°$ fits almost exactly the experimental one. This indicates that the value of the angle of twist θ between the planes of the two naphtyl groups is probably lower than 10°.

The values of θ which give the accordance between the experimental and computed spectra of the three molecules containing a phenyl group are of course much greater. They are 34° 15′ and 46° 15′ for 1-phenylnaphtalene and 2-phenylnaphtalene respectively and increase to 60° for 9,10-diphenylanthracene which is well-known as a typical case of steric hindrance.

These results seem to be quite satisfactory. It is obvious that the rotation of a phenyl group is easier than that of a naphtyl group, because of the smaller size of the former. It might also be predicted that the value of θ should be maximum for

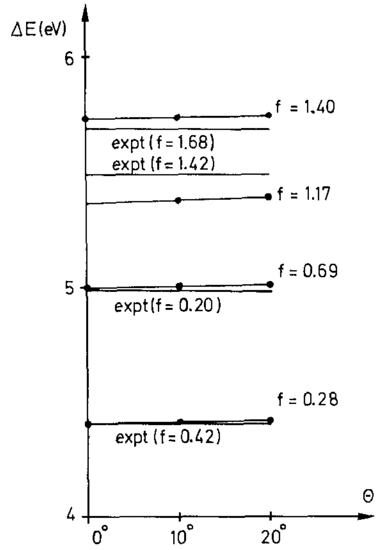


Fig. 1. Singlet transition energies and oscillator strengths in 1,2′-dinaphtyl as a function of θ

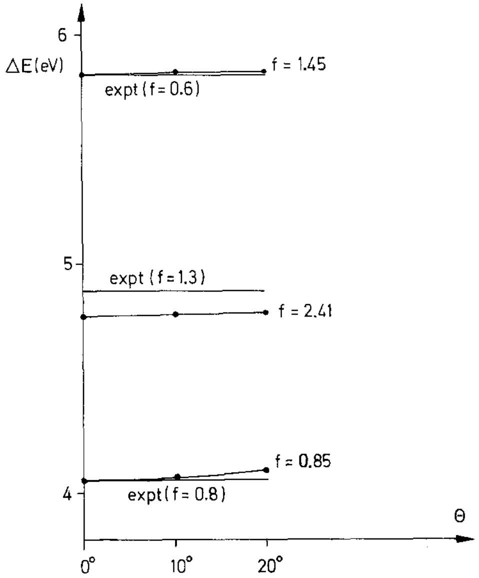
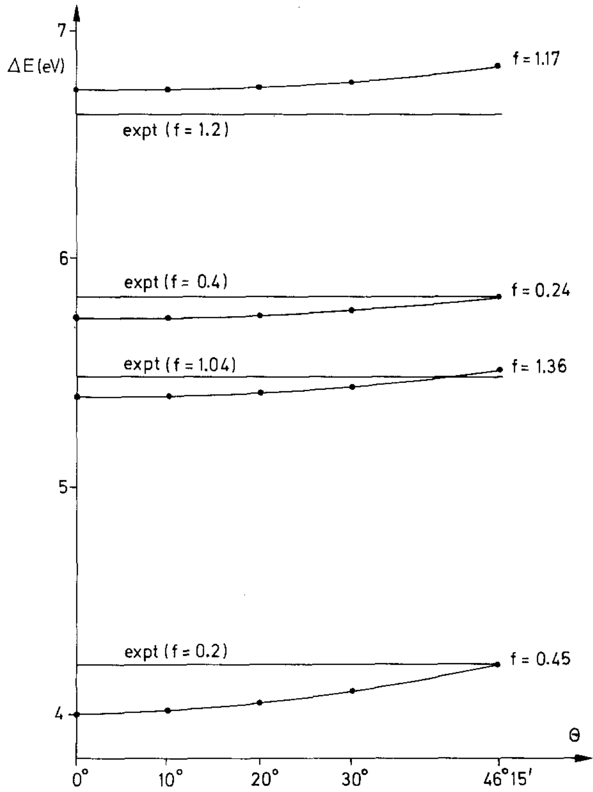


Fig. 2. Singlet transition energies and oscillator strengths in 2,2′-dinaphtyl as a function of θ



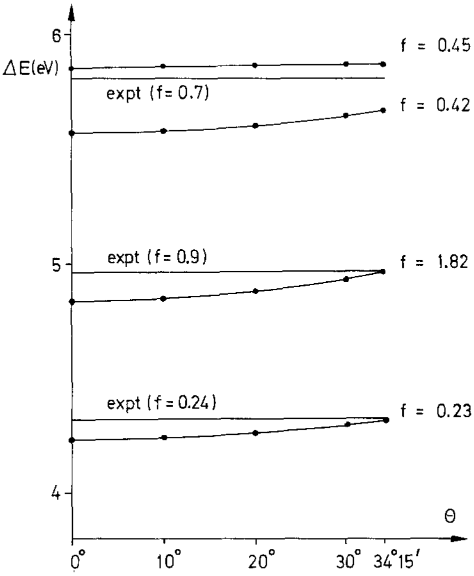


Fig. 4. Electronic spectrum of 2-phenylnaphtalene as a function of θ

Fig. 3. Electronic spectrum of 1-phenylnaphtalene as a function of θ

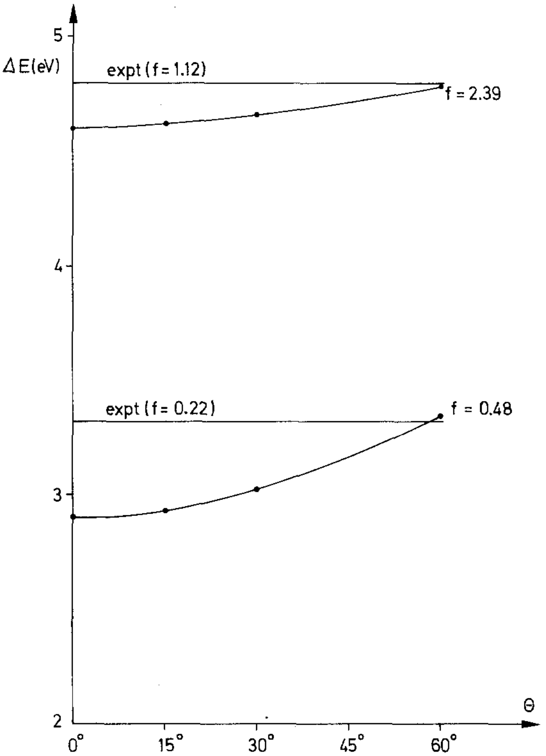
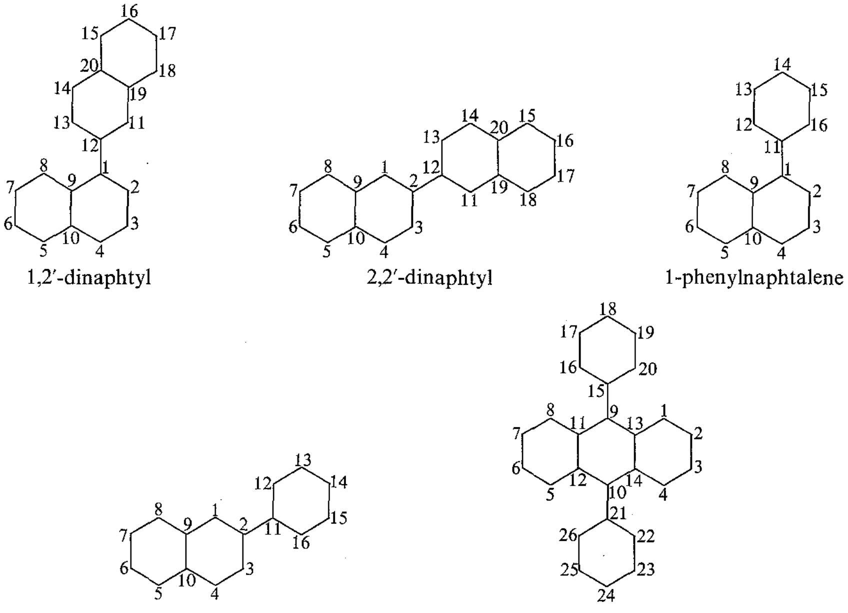


Fig. 5. Electronic spectrum of 9,10-diphenylanthracene as a function of θ



1,2′-dinaphtyl

2,2′-dinaphtyl

1-phenylnaphtalene

2-phenylnaphtalene

9,10-diphenylanthracene

Fig. 6. Numbering scheme

9,10-diphenylanthracene, because the repulsion which occurs between the phenyl group and the main part of the molecule is greater than in the phenylnaphtalenes.

Chen-Hanson Ting [2] is now estimating the angle of twist in 9,10-diphenylanthracene for purposes of fluorescence studies. Unfortunately, his conclusions are yet unpublished and there is no experimental information available at present on the geometry of such molecules.

The calculations were performed on a CDC 3600 computer, using a modified version of the original SCF MO CI program written in Fortran IV by Bloor and Gilson and distributed by the QCPE organization [19].

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