

INTRAMOLECULAR ORBITAL INTERACTIONS IN AND CONFORMATION OF
N,N'-DIPHENYLCARBODIIMIDE STUDIED BY PHOTOELECTRON SPECTROSCOPY

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Abstract: The intramolecular orbital interactions in N,N'-diphenylcarbodiimide were revealed by photoelectron spectroscopy and the phenyl rings in this compound were found to be twisted by ca. 25° from the perpendicular model.

Carbodiimide group is interesting because the N=C=N part is linear and has two π -systems perpendicular and equivalent to each other. In this work the photoelectron spectra of N,N'-diphenylcarbodiimide (DPC) and N-methyl-N'-phenylcarbodiimide (MPC) were measured in order to reveal the mechanism for the orbital interactions among the phenyl group e_{1g} -like π orbitals and the two π -systems of the N=C=N group. The geometrical structure of DPC was assumed to be of C_2 symmetry from its dipole moment.¹⁾

Compounds, DPC and MPC, were synthesized according to the procedures described formerly.²⁾ The gas phase He I photoelectron spectra of these compounds were measured on an instrument described before.^{3,4)} Xe gas was used as the internal reference standard for the calibration of the energy scales.

The photoelectron spectra of DPC and MPC are shown in Figure 1. The vertical ionization energies (E_{iv}) of these compounds obtained from their photoelectron spectra are given in Figure 2. The 8.9 eV band of DPC is rather weak and at the first glance its presence may not be so apparent as that of the first band, but from the careful repeated measurements the 8.9 eV

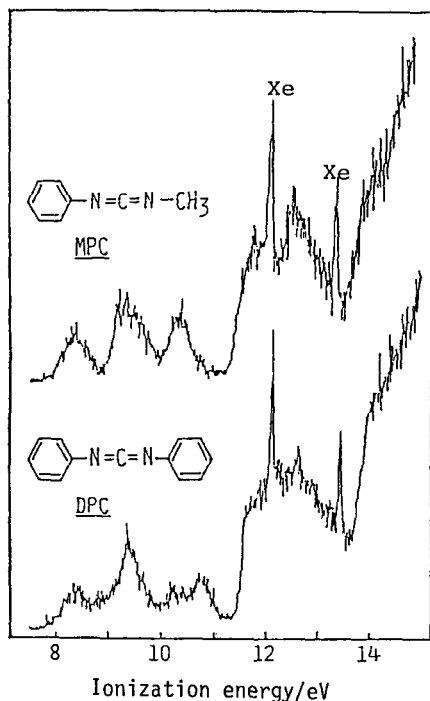


Figure 1. He I photoelectron spectra of N-methyl-N'-phenylcarbodiimide (MPC) and N,N'-diphenylcarbodiimide (DPC).

band has been concluded to be intrinsic for DPC. In the case of MPC, roughly speaking, the observed 8.41 and 10.45 eV bands correspond to the ionizations from the MO's formed by the interaction between the benzene ring $e_{1g}(S)$ -like orbital⁵⁾ and one of the doubly degenerate highest occupied π orbitals of the N=C=N group. From the comparison of the spectrum of MPC with that of DPC the 9.38 eV band of MPC is ascribed to the ionization from the $e_{1g}(A)$ -like π orbital⁵⁾ localized on the benzene ring, and the 9.59 eV band to the ionization from one of the doubly degenerate highest occupied π orbitals of the N=C=N group. This assignment is supported by the PPP type⁶⁾ MO calculation of MPC in conjunction with Koopmans' theorem⁷⁾ except for the locations of the second and third bands.

Now let us move to the case of DPC. The band observed at 9.37 eV is twice as strong as the other four low energy bands (see Figures 1 and 2), and this 9.37 eV band is ascribed to the ionizations from the doubly degenerate MO's localized on the benzene rings, their origins being the benzene ring $e_{1g}(A)$ type orbitals. According to the PPP type calculation of DPC for the C_2 structure with two phenyl rings perpendicular to each other, three doubly degenerate lower energy bands are predicted to appear at around 9.19, 10.28 and 11.24 eV. The 9.19 eV and the 11.24 eV bands correspond to the MO's formed by the mixings of the benzene ring $e_{1g}(S)$ -like orbitals and the two highest occupied π orbitals of the N=C=N group. However, the observed photoelectron spectral bands corresponding to the calculated 9.19 and 11.24 eV

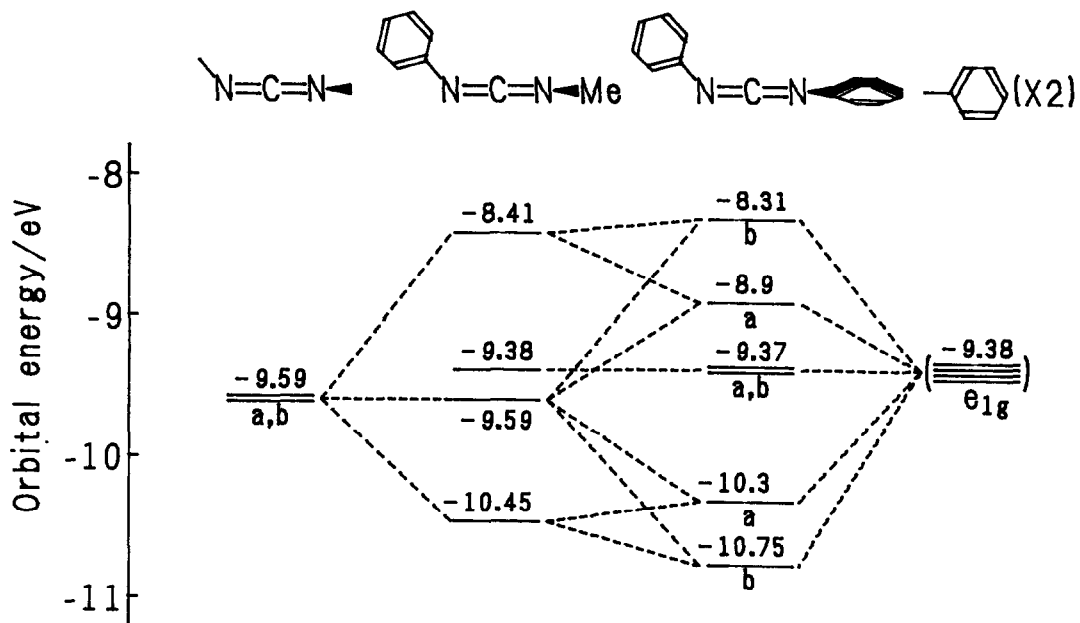


Figure 2. Experimental orbital energy diagram.

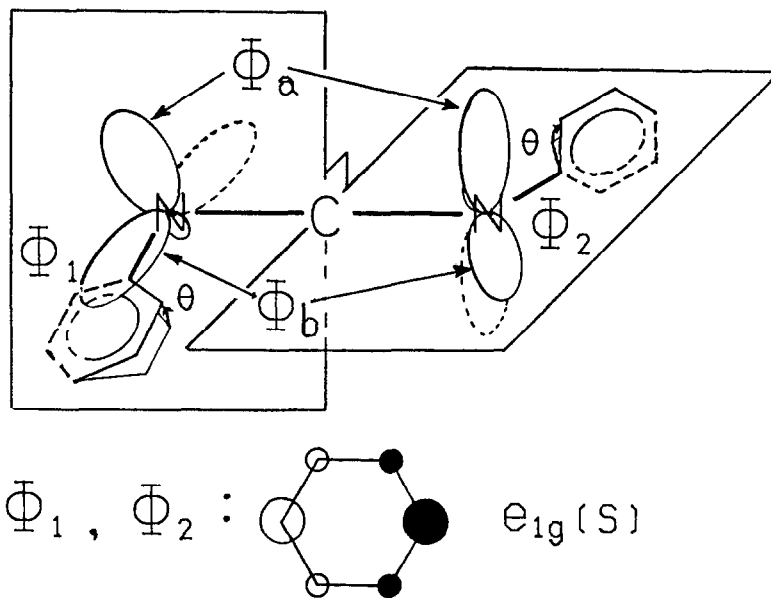


Figure 3. The group orbitals of DPC used in the LCGO calculation.

bands are split by ca.0.5 eV, severally. These results suggest that the two phenyl rings are not completely perpendicular to each other in DPC, but slightly twisted.

In order to estimate the twist angles of the two phenyl rings in DPC in the above sense, a simple LCGO model calculation parameterized using the experimental E_{iv} 's of MPC was carried out for DPC. In the LCGO calculation, the molecular orbitals of DPC are approximated by linear combinations of four group orbitals, ϕ_1 , ϕ_2 , ϕ_a and ϕ_b shown in Figure 3. The matrix elements H_{11} and H_{22} are assumed to be -9.38 eV from the above mentioned $e_{1g}(A)$ -like orbital energy, and H_{aa} and H_{bb} to be -9.59 eV from the N=C=N localized orbital energy. The resonance integrals H_{1a} , H_{2b} , etc. are estimated from the energy separation between the first and the fourth bands of DPC. Here, $H_{ij} = \int \phi_i H \phi_j d\tau$. The twist angles of the phenyl rings in DPC were thus estimated to be ca.25° by comparing the calculated and observed splittings between the first and sixth bands of DPC.

Finally, it is concluded that the π systems of the two phenyl rings are not perfectly orthogonal to each other, but are interacting through the N=C=N group π systems because of the slight twistings of the phenyl groups by ca.25°. In other words, the two π systems in the N=C=N group are interacting with each other through terminal phenyl ring π systems. Further detailed studies are now in progress.

References and notes

- 1) F. Feichtmayr and F. Wüerstlin, Ber. Bunsenges. Phys. Chem., 67, 434(1963).
- 2) T. Hoshi, H. Ito, J. Okubo and S. Mori, J. Chem. Soc. Jpn., 5, 671(1983).
- 3) T. Kobayashi, K. Yokota and S. Nagakura, J. Electron Spectrosc. Relat. Phenom., 2, 449(1973).
- 4) T. Kobayashi, T. Kubota and K. Ezumi, J. Am. Chem. Soc., 105, 2172(1983).
- 5) The $e_{1g}(A)$ orbital has nodes at 1- and 4-positions, and the $e_{1g}(S)$ orbital is orthogonal to the $e_{1g}(A)$ orbital.
- 6) T. Hoshi, M. Kobayashi, J. yoshino, M. Komuro, and Y. Tanizaki, Ber. Bunsenges. Phys. Chem., 83, 821(1979).
- 7) T. Koopmans, Physica, 1, 104(1934).

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