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MOLECULAR COMPLEX OF TETRABENZOYLBENZENE AND DIALLENE

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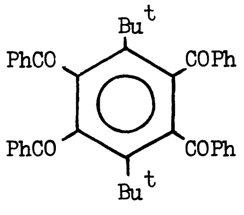
Stable 1:1 complex of tetrabenzoylbenzene (1,2,4,5-tetrabenzoyl-3,6-di-t-butylbenzene, 1) and diallene (meso-3,8-di-t-butyl-1,5,6,10-tetraphenyldeca-3,4,6,7-tetraene-1,9-diyne, 2) was isolated and its structure was studied by X-ray analysis.

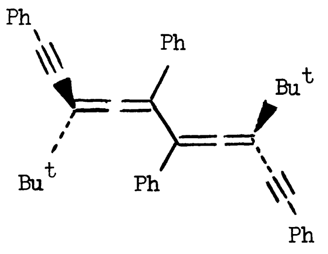
In stable molecular complex, components are bound usually by hydrogen bond or charge transfer interaction. We found that tetrabenzoylbenzene (1,2,4,5-tetrabenzoyl-3,6-di-t-butylbenzene, 1) and diallene (meso-3,8-di-t-butyl-1,5,6,10-tetraphenyldeca-3,4,6,7-tetraene-1,9-diyne, 2) form stable 1:1 complex (3), though neither hydrogen bond nor charge trasfer interaction is considerable between the components, 1 and 2. We now report the isolation and structural study by X-ray analysis of the unusual complex (3).

When an equimolar mixture of 1[1] (mp 234.5-235.5 °C) and 2[2] (mp 123-124 °C) was recrystallized from acetone, 1:1 complex (3) (mp 188 °C) was formed as colorless prisms in almost quantitative yield. IR spectrum of 3 in solid state is different from that of a 1:1 crystalline mixture of 1 and 2. In solution, however, 3 is dissociated into the components.

Because dl-diallene (4)[2] does not form such complex, conformation of the diallene may be an important factor for the formation of complex. Structure of 3 was studied by X-ray analysis. The crystals of 3 are monoclinic, space group I2/c with a = 29.553, b = 10.986, c = 20.648 Å, β = 93.84°, and Z = 4 (half formula units in an asymmetric unit). Intensity data were collected on a Rigaku automated four-circle diffractometer using Ni-filtered Cu Kα radiation and θ - 2θ scanning mode. A total of 2661 independent reflections were obtained with $2\theta \leqq 90°$. The structure was solved by the direct method.[3] The tentative R factor is 0.16 for the 1793 observed reflections.



1



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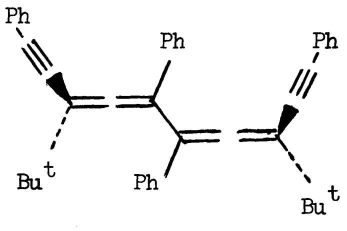

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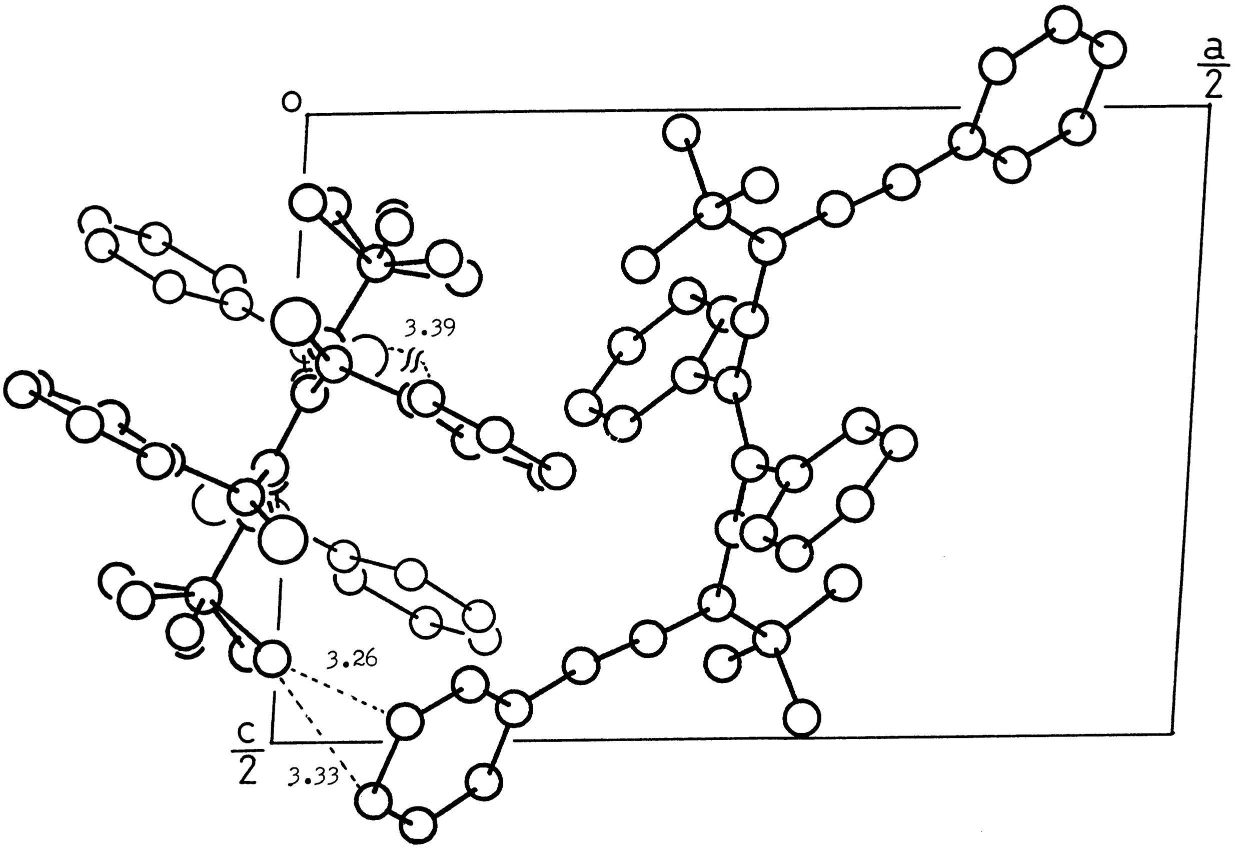

Fig. 1 Molecular structure projected along the b axis

A crystallographic two-fold axis passes through a parallel pair of bonds in central benzene ring of 1, so that the molecule has approximately D_2 point group symmetry.[4] On the other hand, 2 is centrosymmetric; the midpoint of the single bond connecting the two allene skeletons lies on the center of symmetry at (1/4,1/4,1/4). The conformation around this bond is, therefore, transoid form and diallene skeleton is nearly planar so as to make the long π-electron system.

There is no serious intermolecular contact between the molecules of 2. Oxygen atom of 1 is somewhat close (a = 3.39 Å) to the phenyl carbon atom of the equivalent molecule along the b axis (Fig. 1). Short intermolecular distances are those between the t-butyl group of 1 and the phenyl group of 2 (b = 3.26 Å, c = 3.33 Å). These might, however, be regarded as simple van der Waals contacts, and there is no intermolecular π-bond overlap which is usually observed in the charge transfer complex.

REFERENCES AND NOTES

1) F. Toda, N. Dan, K. Tanaka, and Y. Takehira, J. Am. Chem. Soc., 99, 4529 (1977).
2) F. Toda and Y. Takahara, Bull. Chem. Soc. Jpn., 49, 2511 (1976).
3) J. Karle and I. L. Karle, Acta Crystallogr., 21, 849 (1966).
4) This is due to the rotational disorder of t-butyl groups of 1 in this crystal structure.

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