

MOLECULAR COMPLEX OF TETRABENZOYL BENZENE AND DIALLENE

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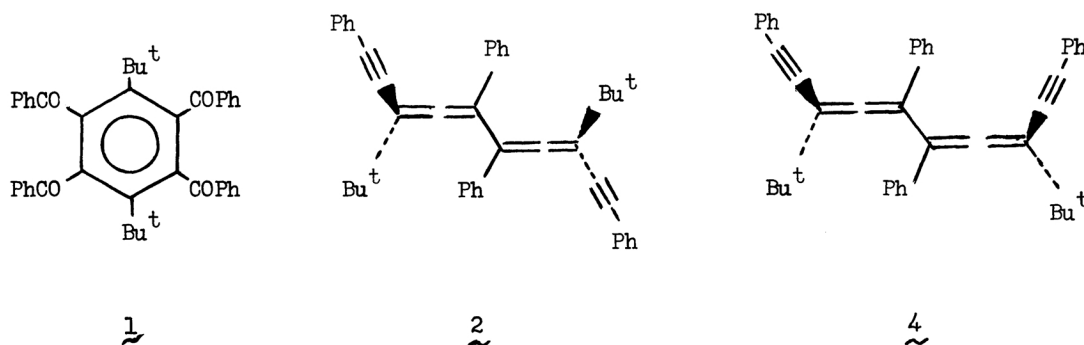
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Stable 1:1 complex of tetrabenzoylbenzene (1,2,4,5-tetrabenzoyl-3,6-di-*t*-butylbenzene, 1) and diallene (meso-3,8-di-*t*-butyl-1,5,6,10-tetraphenyldeca-3,4,6,7-tetraene-1,9-diyne, 2) was isolated and its structure was studied by X-ray analysis.

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 transfer 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 1¹⁾ (mp 234.5-235.5 °C) and 2²⁾ (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, $\beta = 93.84^\circ$, 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 K α radiation and $\theta - 2\theta$ scanning mode. A total of 2661 independent reflections were obtained with $2\theta \leq 90^\circ$. The structure was solved by the direct method.³⁾ The tentative R factor is 0.16 for the 1793 observed reflections.



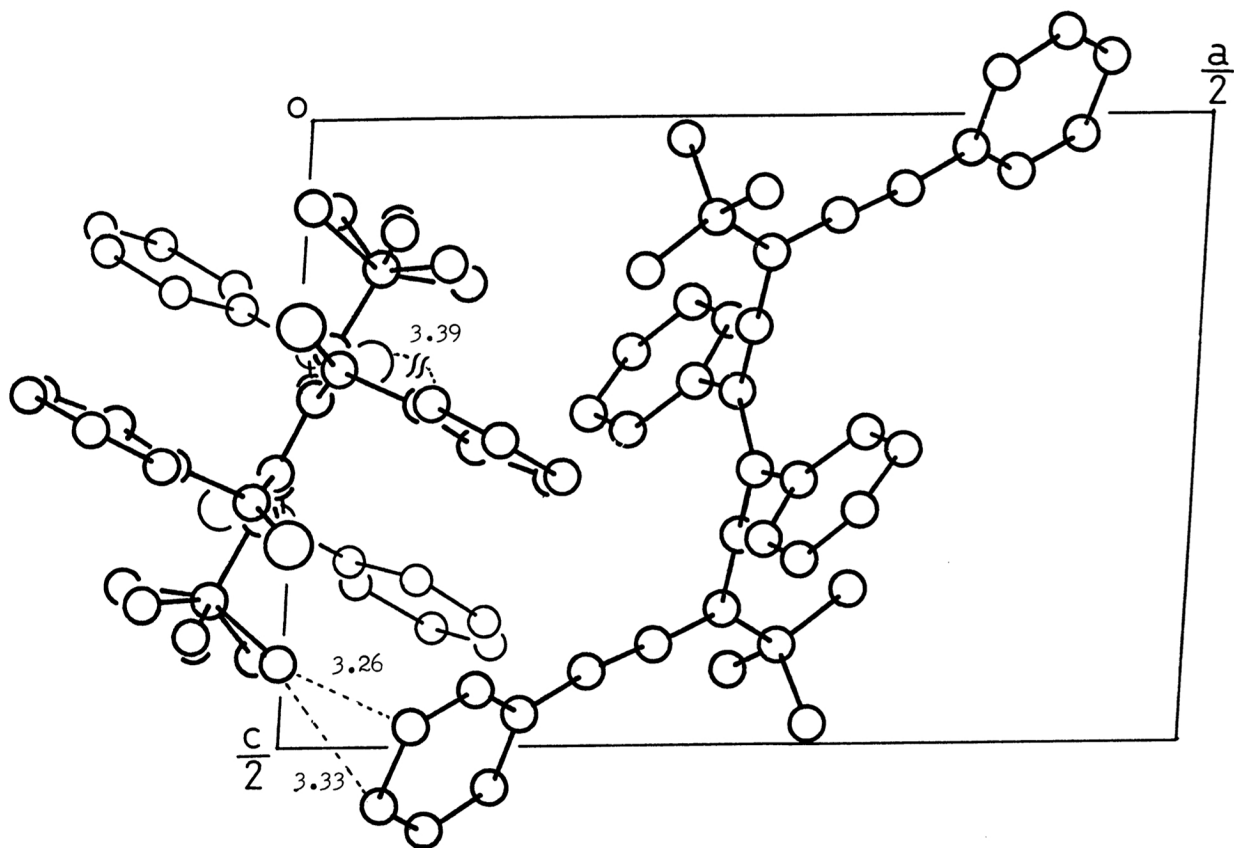


Fig. 1 Molecular structure projected along the b axis

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 ($a = 3.39 \text{ \AA}$) 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 ($b = 3.26 \text{ \AA}$, $c = 3.33 \text{ \AA}$). 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

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- 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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