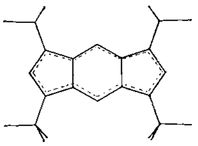
Equilibrium Structure, Stabilized Transition State, or Disorder in the Crystal? Studies of the Antiaromatic Systems Tetra-*tert*-butyl-*s*-indacene and Tetra-*tert*-butylcyclobutadiene by Low-Temperature Crystal Structure Analysis**

By *Jack D. Dunitz*,* *Carl Krüger*, *Hermann Irngartinger*, *Emily F. Maverick*, *Yu Wang*, and *Matthias Nixdorf*

The crystal structure of 1,3,5,7-tetra-*tert*-butyl-*s*-indacene **1** as determined at room temperature[1] shows effective D_{2h} symmetry of the carbon skeleton. Similarly, the presence of only four ^{13}C-NMR signals that show no perceptible line broadening down to $-130\,^{\circ}$C for the twelve C atoms of the perimeter is consistent either with a very low energy barrier between the valence isomers or with a completely delocalized twelve-electron π system. According to calculations[1] (MINDO/3 method), the energy barrier is only about 8 kJ mol^{-1} for the tetrasubstituted molecule **1**, although it is considerably larger for the parent hydrocarbon.[2]



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We now report results of a new, more accurate low-temperature (100 K) X-ray analysis of **1**, which substantiate and extend these indications.[3,4] Although the (crystallographic) molecular site symmetry is only C_i ($\bar{1}$), the molecular geometry (Fig. 1) shows no significant deviations from D_{2h} symmetry.

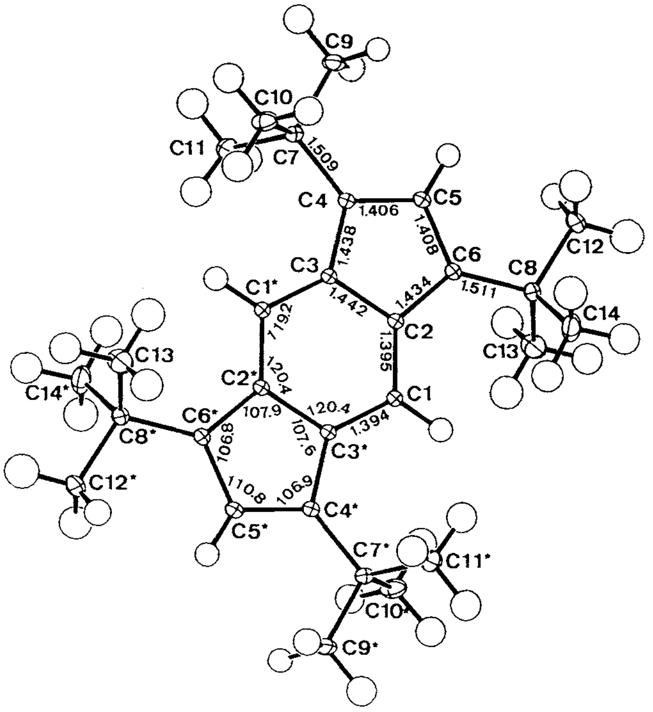

Fig. 1. ORTEP [27] drawing of **1** at 100 K; parameters from the HO refinement [3]. Bond lengths [10^2 pm] and angles [°] are indicated. Ellipsoids are scaled to enclose 50% probability.

Moreover, as described below, a detailed analysis of the anisotropic displacement parameters U^{ij} (ADPs)[5] of the carbon atoms gives no evidence for disorder between two sets of atomic positions for the skeletal atoms. We conclude that either the equilibrium structure of **1** has D_{2h} symmetry with a localized π system or we are observing not the ground-state molecular structure in the crystal but rather the transition state for the valence isomerization, which may be stabilized by crystal packing forces. The example of biphenyl, planar in its crystal structure, nonplanar as a free molecule, can serve as a precedent.[7]

Analysis of the ADPs with *Trueblood*'s THMA program[8] leads to the following indications:

(1) Calculation of mean-square displacement amplitudes (MSDAs)[9] along all interatomic vectors shows that the molecule does not behave as a rigid body in the crystal. The MSDAs between nonbonded pairs of atoms—and indeed the ellipsoids in Figure 1—reveal appreciable motions of the *tert*-butyl groups relative to the indacene skeleton. On the other hand, the rigid-bond criterion[10] is satisfied reasonably well, especially for the indacene skeleton, for which $\langle\Delta(\text{MSDA})^2\rangle^{1/2} = 7$ pm^2.

(2) The translational (***T***) and librational (***L***) analysis,[11] including allowance for internal libration of the *tert*-butyl groups about the exocyclic bonds C4–C7 and C6–C8, leads to mean-square libration amplitudes, $\langle\phi^2\rangle$, of 9 and 20 (°)^2, respectively,[12] considerably larger than the eigenvalues of the **L** tensor (4.9, 0.9, 0.4 (°)^2, with the major eigenvalue approximately along the long axis of the molecule).[13]

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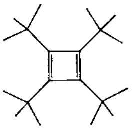
(3) Although the above model leads to reasonable agreement between observed and calculated U tensors ($\langle(\Delta U^{ii})^2\rangle^{1/2} = 15$ pm^2), the residual discrepancies show systematic features. In the direction perpendicular to the ring plane, U_{obsd} is significantly larger than U_{calcd} for the ring atoms C2, C3, and especially C5 ($\Delta U^{33} = 51$ pm^2); for C7 and C8, the reverse is true. Thus the model tends to ascribe too much motion to the quaternary C atoms C7 and C8, and too little to the ring atoms that are not attached to *tert*-butyl groups. This suggests that the ring atoms (especially C5) are moving in a direction perpendicular to the plane. Allowance for out-of-plane bending or buckling of the ring skeleton, as inferred in a variable-temperature study of naphthalene,[15] would reduce these discrepancies. Within the molecular plane there are no significant differences between U_{obsd} and U_{calcd} components for the ring atoms, whereas in an averaged structure involving superposition of two valence isomers with localized single and double bonds, we would expect $U_{\mathrm{obsd}} > U_{\mathrm{calcd}}$ to allow for the effect of disorder.[16] If the observed structure were such a superposition, the two sets of atomic positions could not differ from the averaged positions by more than about 3 pm.

The observed structure, if it is indeed the transition state for interconversion of the free molecules, may be stabilized relative to the structures with localized bonds by better packing of the *tert*-butyl groups. Model calculations suggest that the packing energy would be reduced by about 4 kJ mol^{-1} per *tert*-butyl group for the small in-plane displacements of these groups that would be associated with the reorganization of the indacene skeleton.

In contrast, a comparable analysis of the ADPs from a low-temperature study of tetra-*tert*-butylcyclobutadiene **2**[17] shows that in this crystal at 123 K there is still residual disorder of the atoms of the central four-membered ring, corresponding to the coexistence of both valence isomers (although not in equal amounts).



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The room-temperature X-ray analysis of **2** led to a structure in which the sides of the slightly nonplanar four-membered ring were almost equal (146.4 and 148.3 pm).[18] This result was in conflict with those obtained for other cyclobutadiene derivatives where much larger differences (14–26 pm) between the ring bonds were observed.[19] On the basis of quantum-mechanical model calculations, *Borden* and *Davidson*[20] suggested that the bulky *tert*-butyl groups could exert a considerable "quadratization effect," but this was countered by *Ermer* and *Heilbronner*,[21] who argued from photoelectron spectroscopic evidence and force-field calculations that **2** must have a rectangular structure with appreciably different ring bond lengths. They proposed that the nearly square arrangement of the ring atoms found in the room-temperature analysis did not correspond to the actual molecular structure but rather to averaged atomic positions resulting from disorder among two rectangular structures. Indeed, ring bond lengths found in the subsequent low-temperature crystal structure analysis at 123 K were different (144.1 and 152.7 pm),[17] but the question of whether residual disorder was still present at this temperature was left open. From a detailed analysis of the anisotropic displacement parameters U^{ij}[5] of the carbon atoms in the 123 K structure, we now conclude that residual disorder is indeed still present at this temperature. The results are compatible with an averaged superposition of two mutually perpendicular rectangular rings with sides approximately 160 and 134 pm,[22] and with one orientation several times more probable than the other.

ADPs from the 123 K structure determination were analyzed, as for the indacene derivative **1**, with THMA.[8] Standard deviations of $\boldsymbol{U}$ tensor components are of the order of 5 pm^2. Casual inspection of the probability ellipsoids (Fig. 2) shows that those of the methyl group carbon atoms are systematically larger than those of the other atoms. Calculation of MSDAs[9] along interatomic vectors shows that in contrast to the indacene derivative **1** the rigid-bond criterion[10] is not obeyed for **2**. For example, for the C1–C6 bond Δ(MSDA) is 19 pm^2. This in itself is an indication of possible disorder. However, MSDA differences between nonbonded pairs of atoms are much larger (up to 100 pm^2) and indicate appreciable motions of the *tert*-butyl groups relative to the inner ring.[24]

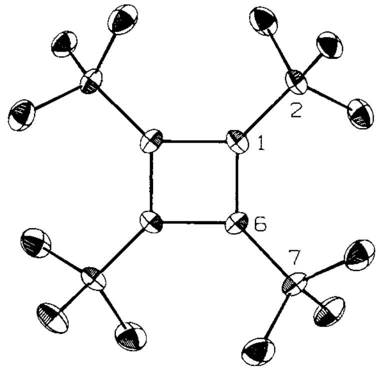

Fig. 2. ORTEP [26] drawing of **2** at 123 K. Ellipsoids are scaled to enclose 50% probability. Hydrogen atoms are omitted for clarity.

The $\boldsymbol{T}$, $\boldsymbol{L}$, and screw tensor ($\mathbf{S}$) analysis, including internal libration of the two independent *tert*-butyl groups about the C1–C2 and C6–C7 bonds, leads to mean-square libration amplitudes $\langle\phi^2\rangle$ of 14 and 23 (°)^2 for the two internal motions, respectively.[12] These are several times larger than the eigenvalues of the $\boldsymbol{L}$ tensor (4.4, 2.4, 2.2 (°)^2, with the lowest value along the crystallographic twofold rotation axis; the molecule has effective D_2 symmetry but only one of the symmetry elements is imposed by the space group).[25]

The residual discrepancies between observed and calculated $\boldsymbol{U}$ tensors show systematic features. One of these is the striking excess of 51 and 31 pm^2 of the observed over the calculated tangential components of C1 and C6 (Table 1). This feature cannot be attributed to underestimation of the overall molecular libration (this would affect the outer atoms rather than the inner ones), but it is qualitatively in

Table 1. Calculated and observed mean-square displacement amplitudes [pm^2] for the ring atoms C1 and C6 in **2** along the tangential, radial, and ring-normal directions.

	Observed	Calculated
C1	221, 126, 170	170, 166, 154
C6	210, 126, 164	179, 157, 145

accord with the disorder model proposed by *Ermer* and *Heilbronner* (see Fig. 1 in Ref. [21]). In the crystal it is not necessary that the two perpendicular orientations of the rectangular ring have a common center (indeed, the abovementioned Δ(MSDA) of 19 pm^2 between C1 and C6 suggests that they do not). However, if we wish to make a rough estimate of the proportions of major and minor orientation present, it simplifies the argument somewhat if we assume this condition to be satisfied and use the averaged tangential MSDA excess of 41 pm^2.

For equal occupancy of the two perpendicular orientations of a rectangular ring with sides of 134 and 160 pm[22] and a common center, we expect an excess MSDA of 84 pm^2 in the tangential direction (in agreement with *Ermer* and *Heilbronner*'s estimate of 80 pm^2[21]). For other occupancy factors p, the excess is then $336p(1-p)$ and hence $p \approx 0.86$ for the observed excess MSDA of 41 pm^2 at 123 K.[26]

These examples, 1,3,5,7-tetra-*tert*-butyl-*s*-indacene with indications of delocalization consistent with a stabilized transition state between two valence isomers, and tetra-*tert*-butylcyclobutadiene with evidence for disorder among the two isomers, show how ADPs derived from high-quality diffraction data can provide information about the nature and extent of mean displacements of atoms from their equilibrium positions and hence allow differentiation among alternative models compatible with these positions.

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1, 101998-70-3; **2**, 66809-05-0.

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[2] For HMO arguments showing that **1** should have a more delocalized π system than the unsubstituted *s*-indacene, see also E. Heilbronner, Z.-z. Yang, *Angew. Chem. 99* (1987) 369; *Angew. Chem. Int. Ed. Engl. 26* (1987) 360.

[3] Crystal structure of **1**: monoclinic, space group $P2_1/n$, $Z=2$, $a=970.0(3)$, $b=1174.6(3)$, $c=1085.8(2)$ pm, $\beta=107.67°$, $T=100$ K, $\rho_{calcd}=1.06$ g cm^{-3}, $Mo_{K\alpha}$ radiation ($\lambda=71.069$ pm), $\mu=0.52$ cm^{-1} (no absorption correction applied), 22565 measured reflections, reduced to 5636 independent reflections ($R_{av}=0.022$), 4383 observed ($I>2\sigma(I)$), 207 parameters refined, $R=0.043$, $R_w=0.039$, $R_{HO}=0.030$ ($\sin\theta/\lambda>0.0065$ pm^{-1}). Measured reflections: $\pm h$ $\pm k$ l $0<\theta<42°$, $\psi=0°$; $\pm h$ $\pm k$ l $0<\theta<42°$, $\psi=15°$; $\pm h$ $\pm k$ l $0<\theta<16°$, $\psi=-45/45°$. Normal data set 45 kV/32 mA; attenuated reflection set 50 kV/8 mA, 40 kV/8 mA. Further details of the crystal structure investigation may be obtained on request from the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2 (FRG), by quoting the number CSD-52900, the names of the authors, and the complete citation of the article.

[4] We thank Prof. *K. Hafner* for supplying samples and Prof. *H. J. Lindner* for sending the room-temperature crystal data and other information.

[5] U^{ij} are the components of the symmetric second-order tensor $\boldsymbol{U}$ which defines the matrix of second moments of the probability distribution function for each atom. They are obtained along with positional coordinates of the atoms by least-squares analysis of the experimental structure amplitudes from X-ray or neutron diffraction. The interpretation of ADPs is discussed in some detail in a recent review [6].

[6] J. D. Dunitz, V. Schomaker, K. N. Trueblood, *J. Phys. Chem.* (1988), in press.

[7] W. R. Busing, *Acta Crystallogr. Sect. A 39* (1983) 340.

[8] K. N. Trueblood, *Acta Crystallogr. Sect. A 34* (1978) 950. Several versions of this program are in circulation, the latest being THMA 11.

[9] The mean-square displacement amplitude in the direction of a unit vector $\boldsymbol{n}$ is given by $\boldsymbol{n}^T\boldsymbol{U}\boldsymbol{n}$, where the components of $\boldsymbol{n}$ are referred to unit-length reciprocal basis vectors.

[10] F. L. Hirshfeld, *Acta Crystallogr. Sect. A 32* (1976) 239.

[11] For the analysis of **1** described here, the screw tensor $\boldsymbol{S}$ vanishes because of the molecular site symmetry. In the $\boldsymbol{T}$, $\boldsymbol{L}$ analysis we used the parameters from refinement of the full data set, but results obtained with parameters from the HO refinement [3] are practically the same.

[12] As discussed by *V. Schomaker* and *K. N. Trueblood, Acta Crystallogr. Sect. A 40* Suppl. (1984) C-339 (see also [6]), these values correspond strictly not to $\langle\phi^2\rangle$ but to $\langle\phi^2\rangle+\langle\phi\lambda^{\parallel}\rangle$, where $\langle\phi\lambda^{\parallel}\rangle$ is the parallel component of the overall molecular libration. However, since the overall libration is here small compared with the internal libration, their quadratic average must also be small.

[13] Values of mean-square libration amplitudes $\langle\phi^2\rangle$ were also estimated by numerical integration of

$$\int \phi^2 \exp(-V(\phi)/RT)\,\mathrm{d}\phi \Big/ \int \exp(-V(\phi)/RT)\,\mathrm{d}\phi$$

where $V(\phi)$ was obtained from calculated potential energy curves [14] for step-by-step rotation of the *tert*-butyl groups about the appropriate axes without relaxation of the surrounding crystal structure. The calculated values of $\langle\phi^2\rangle$ are about 50% too small, but larger for C6–C8 than for C4-C7, as found in the ADP analysis.

[14] U. Shumueli, P. A. Kroon, *Acta Crystallogr. Sect. A 30* (1974) 768.

[15] C. P. Brock, J. D. Dunitz, *Acta Crystallogr. Sect. B 38* (1982) 2218.

[16] The U components arising from this kind of disorder would not be completely absorbed in a model involving additional librational motion.

[17] H. Irngartinger, M. Nixdorf, *Angew. Chem. 95* (1983) 415; *Angew. Chem. Int. Ed. Engl. 22* (1983) 403.

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[19] a) H. Irngartinger, H. Rodewald, *Angew. Chem. 86* (1974) 783; Angew. Chem. Int. Ed. Engl. 13 (1974) 740; b) L. R. J. Delbaere, M. N. G. James, N. Nakamura, S. Masamune, *J. Am. Chem. Soc. 97* (1975) 1973.

[20] W. T. Borden, E. R. Davidson, *J. Am. Chem. Soc. 102* (1980) 7958.

[21] O. Ermer, E. Heilbronner, *Angew. Chem. 95* (1983) 414; *Angew. Chem. Int. Ed. Engl. 22* (1983) 402.

[22] These bond lengths are chosen to agree with values found in other cyclobutadiene derivatives [18, 19a, 23].

[23] H. Irngartinger, M. Nixdorf, N. H. Riegler, A. Krebs, H. Kimling, J. Pocklington, G. Maier, K.-D. Malsch, K.-A. Schneider, *Chem. Ber.*, in press.

[24] R. E. Rosenfield, K. N. Trueblood, J. D. Dunitz, *Acta Crystallogr. Sect. A 34* (1978) 828.

[25] Calculations [13] reproduce the difference in internal motion between these groups but the values of $\langle\phi^2\rangle$ are too small. However, since the intramolecular overcrowding among the *tert*-butyl groups is so severe, allowance for correlated motion will certainly need to be included in a more realistic model.

[26] From the observed bond lengths of 144.1 and 152.7 pm we would estimate $p \approx 0.7$, assuming the same rectangular ring. For a more thorough discussion of the disorder on Δ(MSDA) values see K. Chandrasekhar, H. B. Bürgi, *Acta Crystallogr. Sect. B 40* (1984) 387.)

[27] C. K. Johnson: ORTEP-II: A FORTRAN Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations (report ORNL-5138), Oak Ridge National Laboratory, Oak Ridge, TN, USA 1976.

Reaction of 1,3-Azaphosphinines with 2-*tert*-Butyl-1-phosphaethyne: 9-Aza-2,4,6-triphosphatetracyclo[5.3.0.$0^{2,4}$.$0^{3,6}$]deca-8,10(1)-diene

By *Gottfried Märkl*,* *Stefan Dietl*, *Manfred L. Ziegler*, and *Bernd Nuber*

Recently, we reported the synthesis of 1,3-azaphosphinines **1** from 3-azapyrylium salts by O/P exchange with $(Me_3Si)_3P$.[1]

In contrast to phosphinines, which only undergo Diels-Alder reactions with highly reactive alkyne dienophiles (e.g., hexafluorobutyne) under drastic reaction conditions to give 1-phosphabarrelenes,[2] 1,3-azaphosphinines **1** react with all alkynes so far investigated even under mild condi-

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