

torsion angles are shown in Table 2.\* Fig. 1 shows the crystal structure and the numbering of the atoms and Fig. 2 the crystal packing. The angle of intersection between plane *A*, defined by C(1), C(2) and C(3) and plane *B*, defined by C(1), C(7) and C(6), is 148.3° ( $\alpha_1$ ), whereas the angle of intersection between plane *A* and plane *C*, defined by C(2), C(1) and C(7), is 9.9° ( $\alpha_2$ ) and that between planes *B* and *C* is 36.4° ( $\alpha_3$ ). These values are close to those ( $\alpha_1 = 145.2$ ,  $\alpha_2 = 14.1$  and  $\alpha_3 = 39.6^\circ$ ) of 10,11-dihydro-dibenzo[*a,d*]cyclohepten-5-one (3) (Weissensteiner, Hofer & Wagner, 1988). The dihedral angle between bonds C(3)—C(4) and C(5)—C(6) is 74.3°, whereas the corresponding angle for (3) is reported to be 81.8° (Weissensteiner, Hofer & Wagner, 1988). Thus, the molecule is saddle-like in shape with  $C_1$  symmetry.

In solution, the carbonyl group of (1) flips freely via a  $C_2$  symmetrical transition state and the bond twisting at the  $sp^3$  carbons occurs between two half-

\* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond distances and angles involving H atoms, and r.m.s. amplitudes of thermal vibration have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53084 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

boat forms via a  $C_3$  symmetrical transition state. The Gibbs energy of this bond twisting is 63–65 kJ mol<sup>-1</sup> at 298 K (Mori, Kubota & Takeshita, 1989), whereas the interconversion barriers for 10,11-dihydro-5*H*-dibenzo[*a,d*]cycloheptene derivatives were calculated to be smaller than 29 kJ mol<sup>-1</sup> (Weissensteiner, Hofer & Wagner, 1988). The conformation of (1) in the solid state seems to be similar to that observed in solution.

The X-ray diffraction measurements were made using a CAD-4 diffractometer at the Center of Advanced Instrumental Analysis, Kyushu University.

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## Structure of *trans*-1,6-Diphenyl-3-hexene-1,5-diyne

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**Abstract.**  $C_{18}H_{12}$ ,  $M_r = 228.29$ , monoclinic,  $C2/c$ ,  $a = 24.246$  (3),  $b = 14.214$  (1),  $c = 11.536$  (6) Å,  $\beta = 101.19$  (3)°,  $V = 3899.92$  (3) Å<sup>3</sup>,  $Z = 12$ ,  $D_m = 1.14$ ,  $D_x = 1.17$  g cm<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.54177$  Å,  $\mu = 4.682$  cm<sup>-1</sup>,  $F(000) = 1440$ ,  $T = 293$  K,  $R = 0.052$  for 1807 observed reflections. The asymmetric unit contains one molecule in a general position and a half molecule at a centre of symmetry. The phenyl rings are planar, and for the molecule in a general position, inclined with respect to each other by a dihedral angle of 9.1 (1)°. The C—C bonds in the chain

connecting the two phenyl rings have single-, double- and triple-bond character.

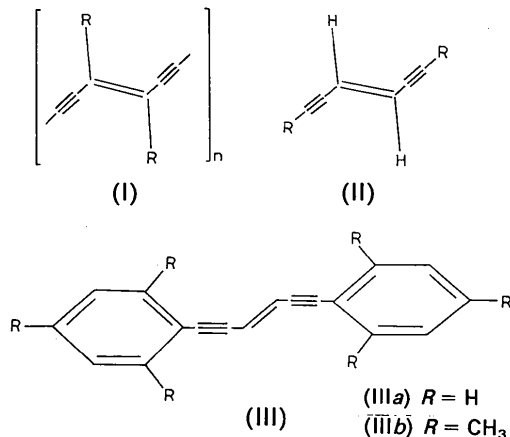
**Introduction.** Conjugated polymers such as polydiacetylene, polyacetylene and poly(*p*-phenylene) have interesting properties resembling those of photoconductors, semiconductors or even metals (Whangbo, Hoffman & Woodward, 1979).

Among these polymers the polydiacetylenes (I) are especially important as they may be obtained as pure single crystals with interesting optical properties. Thus, they change colour under the influence of heat, light or solvents (Chance, Washabaugh & Hupe,

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1985). These changes hitherto have been unexplained and are currently the subject of much speculation. Large substituent groups, where *R* is sulfonate, urethane, alkyl or hydroxyalkyl, greatly reduce the solubilities of the polymers rendering their structures inappropriate for spectral analysis.

To overcome the experimental difficulties, the monomeric enynes (II) are used as model compounds since they possess similar structures and exhibit similar optical behaviour to the polydiacetylenes, but have good solubilities in different solvents (Balcioglu, Ünaleroğlu & Aydın, 1985).



*trans*-1,6-Diphenyl-3-hexene-1,5-diyne, (IIIa), and the corresponding mesityl compound (IIIb), were synthesized and their thermal and optical behaviour investigated. Compound (IIIb) in solution underwent *trans/cis* isomerization under the effect of heat or light. This transformation effects the blue shift and causes a reduction of the intensity of the long-wavelength absorption band. Compound (IIIa) also underwent a *trans/cis* isomerization and showed a reduction of the intensity of the long-wavelength absorption band, but not accompanied by a blue shift. The similar optical behaviour of (IIIb) and *trans*-polydiacetylenes after thermal or photochemical treatment has been attributed to a conformational rotation around certain bonds as a result of steric effects and a concomitant shortening in the extent of conjugation in *Z* isomers of these molecules (Gülce, 1986). The authors aim to clarify the nature of the decrease in conjugation observed in *Z* isomers of (IIIb) and *trans*-polydiacetylenes by structural analysis of various enynes. In this first paper of the series, the structure of the title compound is discussed.

**Experimental.** 4.24 g of 1,2-diiodoethene and 5 g of copper(I) phenylacetylide were dissolved in 100 ml pyridine under dry nitrogen. The reaction mixture was maintained at 368 K for 4 h and then cooled.

Table 1. *Experimental data and structure-refinement parameters*

Method of measuring $D_n$	Flotation in aqueous KI
Crystal shape and size (mm)	Prismatic, 0.3 × 0.3 × 0.8
Diffractometer used and data-collection technique	Four-circle diffractometer (Enraf-Nonius, CAD-4), $\omega$ -2 $\theta$ scan
Number and $\theta$ range (°) of reflections used for measuring lattice parameters	25 reflections with $8 \leq 2\theta \leq 51$
Maximum value of $\sin\theta/\lambda$ (Å <sup>-1</sup> ) reached in intensity measurements	0.617
Ranges of <i>h</i> , <i>k</i> and <i>l</i>	$-1 \leq h \leq 29$ , $-1 \leq k \leq 17$ , $-14 \leq l \leq 14$
Standard reflections and their intensity variation (%) throughout experiment	800, 230, 321; 0,1,0
Number of significant reflections with $I > 3\sigma(I)$	1807
Method used to solve structure	Direct methods
Use of <i>F</i> or <i>F</i> <sup>2</sup> magnitudes in least-squares refinement	<i>F</i>
Parameters refined	315
Values of <i>R</i> , <i>wR</i>	0.052, 0.065
Final residual electron density (e Å <sup>-3</sup> ) for max. and min. peaks	+0.58 and -0.58
Max. ( $\Delta/\sigma$ )	0.02
Source of atomic scattering factors	<i>International Tables for X-ray Crystallography</i> (1974, Vol. IV)
Computer programs used	SHELXS86 (Sheldrick, 1986), CRYSTALS (Watkin, Carruthers & Betteridge, 1985), SNOOPI (Davies, 1983)

300 ml dilute hydrochloric acid was added. The mixture was treated with ether and then washed successively with hydrochloric acid, sodium carbonate solution and water. The ether phase was dried over magnesium sulfate for 24 h, filtered and the ether distilled. The resulting solid was recrystallized from *n*-hexane. After about a week yellow prismatic crystals were obtained.

Experimental data, methods used to solve the structure and other related data and procedures are given in Table 1. Non-H atoms were refined anisotropically and H atoms were located by difference Fourier syntheses and refined isotropically.

Initially a unit weighting scheme was used, but in the final stages of the refinement the weights were assigned using the method described by Carruthers & Watkin (1979), as incorporated into the CRYSTALS package of programs (Watkin, Carruthers & Betteridge, 1985).

**Discussion.** The final atomic coordinates and equivalent isotropic thermal parameters are given in Table 2; interatomic distances and angles for the non-H atoms in the asymmetric unit are listed in Table 3.\*

\* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond distances and angles involving H atoms, and least-squares-planes data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53097 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Atomic coordinates ( $\times 10^4$ ) and isotropic or equivalent isotropic thermal parameters ( $\text{\AA}^2 \times 10^4$ ) with e.s.d.'s in parentheses

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

Molecule 1	x	y	z	$U/U_{eq}$
C1	175 (1)	7879 (2)	4259 (2)	536
C2	502 (1)	7339 (2)	3985 (2)	563
C3	900 (1)	6682 (2)	3702 (2)	619
C4	987 (1)	6528 (2)	2612 (3)	614
C5	1384 (1)	5878 (2)	2336 (2)	579
C6	1710 (1)	5336 (2)	2042 (2)	547
C11	-223 (1)	8524 (2)	4573 (2)	495
C12	-222 (1)	8720 (2)	5763 (2)	625
C13	-600 (1)	9348 (3)	6050 (3)	740
C14	-983 (1)	9789 (2)	5202 (3)	740
C15	-990 (1)	9601 (2)	4017 (3)	760
C16	-614 (1)	8974 (2)	3717 (3)	656
C61	2098 (1)	4699 (2)	1684 (2)	487
C62	2129 (1)	4634 (2)	483 (2)	595
C63	2500 (1)	4012 (2)	142 (3)	692
C64	2841 (1)	3458 (2)	938 (3)	700
C65	2814 (1)	3515 (2)	2123 (3)	756
C66	2446 (1)	4130 (2)	2484 (3)	659

Molecule 2 on centre of symmetry at $\frac{1}{2}, 1, 0$	x	y	z	$U/U_{eq}$
C7	4252 (1)	8724 (2)	1137 (2)	645
C8	4582 (1)	9239 (2)	835 (3)	701
C9	5000 (2)	9855 (2)	538 (3)	803
C71	3868 (1)	8072 (2)	1499 (2)	565
C72	3925 (1)	7819 (2)	2696 (3)	660
C73	3578 (1)	7171 (2)	3032 (3)	716
C74	3163 (1)	6750 (2)	2221 (3)	745
C75	3094 (1)	6990 (2)	1034 (3)	733
C76	3446 (1)	7646 (2)	685 (3)	653

Table 3. Bond lengths ( $\text{\AA}$ ) and bond angles ( $^\circ$ ) with e.s.d.'s in parentheses

C1—C2	1.190 (3)	C14—C15	1.391 (5)
C1—C11	1.428 (3)	C15—C16	1.367 (4)
C2—C3	1.425 (4)	C61—C62	1.405 (3)
C3—C4	1.332 (3)	C61—C66	1.284 (4)
C4—C5	1.415 (4)	C62—C63	1.373 (4)
C5—C6	1.198 (3)	C63—C64	1.360 (4)
C6—C61	1.425 (3)	C64—C65	1.384 (4)
C7—C8	1.186 (4)	C65—C66	1.369 (4)
C7—C71	1.432 (4)	C71—C72	1.407 (4)
C8—C9	1.430 (4)	C71—C76	1.387 (4)
C9—C9C	1.308 (6)	C72—C73	1.354 (4)
C11—C12	1.400 (3)	C73—C74	1.371 (5)
C11—C16	1.385 (4)	C74—C75	1.390 (4)
C12—C13	1.366 (4)	C75—C76	1.376 (4)
C13—C14	1.364 (5)		
C11—C1—C2	179.2 (3)	C6—C61—C62	119.5 (2)
C1—C2—C3	177.8 (3)	C6—C61—C66	122.1 (2)
C2—C3—C4	124.2 (3)	C62—C61—C66	118.5 (2)
C3—C4—C5	124.0 (3)	C61—C62—C63	119.2 (3)
C4—C5—C6	176.7 (3)	C62—C63—C64	121.7 (3)
C5—C6—C61	179.4 (3)	C63—C64—C65	119.6 (3)
C71—C7—C8	177.7 (3)	C64—C65—C66	119.8 (3)
C7—C8—C9	176.7 (4)	C65—C66—C61	121.3 (3)
C8—C9—C9C	123.4 (4)	C7—C71—C72	120.5 (3)
C1—C11—C12	120.2 (2)	C7—C71—C76	121.4 (2)
C1—C11—C16	121.2 (2)	C72—C71—C76	118.1 (2)
C12—C11—C16	118.6 (2)	C71—C72—C73	120.5 (3)
C11—C12—C13	119.6 (3)	C72—C73—C74	121.1 (3)
C12—C13—C14	121.5 (3)	C73—C74—C75	119.8 (3)
C13—C14—C15	119.5 (3)	C74—C75—C76	119.4 (3)
C14—C15—C16	119.6 (3)	C75—C76—C71	121.1 (3)
C15—C16—C11	121.2 (3)		

The structure of the title compound is shown in Fig. 1 and the corresponding molecular packing diagram in Fig. 2.

The unit cell contains 12 molecules of the title compound and the asymmetric unit therefore comprises one complete molecule in a general position, molecule 1, and half of a second molecule which lies on a centre of symmetry at  $\frac{1}{2}, 1, 0$ , molecule 2. The C—C bond lengths in the hexenediyne skeletons of both molecules indicate only a small degree of conjugation; the average values are 1.426 (6), 1.322 (6) and 1.192 (5)  $\text{\AA}$  for single, double and triple bonds respectively. The hexenediyne moieties are planar within experimental error, as are all three phenyl rings in the asymmetric unit. However, in molecule 1 the phenyl rings at C1 and C6 make different dihedral angles with the plane of the olefinic skeleton, whereas for molecule 2 they are constrained by the crystallographic symmetry to be identical. Thus the phenyl ring C61—C66 inclusive lies in the same plane as the olefinic skeleton C1—C6 inclusive with a

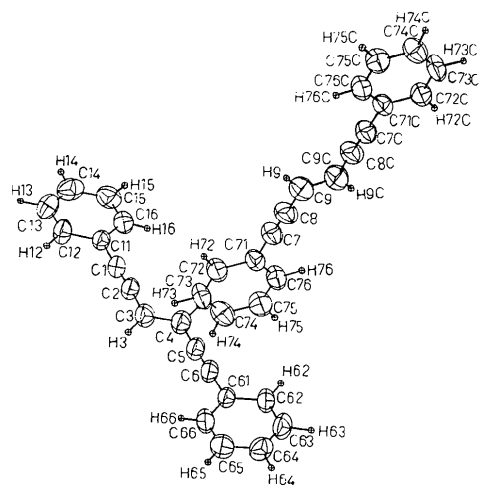


Fig. 1. A SNOOPI (Davies, 1983) drawing of the title molecule, with the atom-numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.

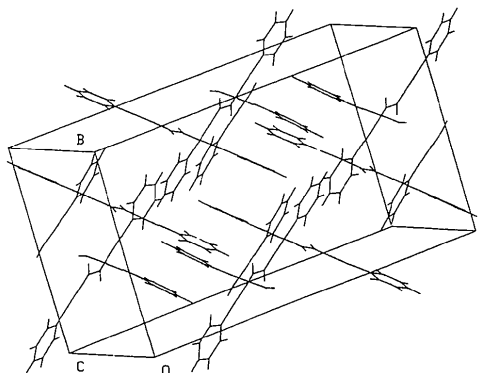


Fig. 2. A perspective view of the crystal packing.

dihedral angle of  $0.3(2)^\circ$ , whereas phenyl ring C11–C16 inclusive is inclined at an angle of  $9.1(2)^\circ$  to this skeleton. In the molecule 2 both phenyl rings are inclined at an angle of  $5.5(2)^\circ$ . The dihedral angles between the phenyl-ring planes are  $9.1(1)$  and  $0^\circ$  for molecules 1 and 2 respectively.

In the unit cell there are no intermolecular contacts which are significantly less than the sum of the respective van der Waals radii.

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### *N*-Adamant-1-yl-*N'*-(2-iodophenyl)guanidinium Chloride

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**Abstract.** *N*-(2-Iodophenyl)-*N'*-(tricyclo[3.3.1.1<sup>3,7</sup>]-decan-1-yl)guanidinium chloride,  $C_{17}H_{23}ClIN_3$ ,  $M_r = 431.75$ , monoclinic,  $P2_1/c$ ,  $a = 11.696(5)$ ,  $b = 20.120(4)$ ,  $c = 7.754(2)$  Å,  $\beta = 95.26(3)^\circ$ ,  $V = 1817(1)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.578$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 1.89$  mm<sup>-1</sup>,  $F(000) = 864$ ,  $T = 295$  K,  $R = 0.071$  for 1169 observed [ $I \geq 3\sigma(I)$ ] reflections. Both the phenyl and the adamantyl groups lie *syn* to the unsubstituted nitrogen of the guanidinium ion. The plane of the phenyl ring is nearly perpendicular to that of the guanidinium group.

**Introduction.** *N,N'*-Di-*ortho*-tolylguanidine and its congeners are highly potent and selective ligands for the haloperidol-sensitive sigma ( $\sigma$ ) receptor (Weber, Sonders, Quarum, McLean, Pou & Keana, 1986; Largent, Wikström, Gundlach & Snyder, 1987). As such, they are of considerable current interest as potential atypical antipsychotic agents, devoid of the severe and long-lasting side effects of currently available antipsychotic neuroleptic drugs (Snyder & Largent, 1989; Largent, Wikström, Snowman & Snyder, 1988; Deutsch, Weizman, Goldman & Morihisa, 1988). In addition, certain *N,N'*-

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diarylguanidines are also potent ligands for the *N*-methyl-D-aspartate/PCP (NMDA/PCP) receptor (Keana *et al.*, 1989). Such compounds have been shown to have potent neuroprotective properties against glutamate-induced neuronal cell death (Cavalheiro, Lehmann & Turski, 1988; Olney, Labruyere & Price, 1989). They hold promise as an entirely new therapeutic tool for the treatment of neurodegenerative symptoms of stroke or heart attack (Choi, 1988).

We have examined the structure–affinity relationships of a large series of *N,N'*-disubstituted guanidines (Scherz *et al.*, 1990). Briefly, *N,N'*-diarylguanidines bearing either iodine or small alkyl substituents (*e.g.* CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>) in the *ortho* or *meta* position bind tightly to the  $\sigma$  receptor and the NMDA/PCP receptor. Replacement of one of the aryl rings with a small saturated carbocycle such as cyclohexyl, norbornyl, or adamantyl completely abolishes binding to the NMDA/PCP receptor, and increases significantly binding to the  $\sigma$  receptor.

We sought to identify the structural requirements of *N,N'*-disubstituted guanidines for potent, selective binding to the  $\sigma$  receptor. To this end we undertook the X-ray crystallographic analysis of one of the most potent and selective  $\sigma$  receptor ligands available from our studies, *N*-adamant-1-yl-*N'*-2-iodo-

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