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CONFORMATIONAL BEHAVIOUR OF 3-PHENYL- AND 3-CARBOMETHOXY-SUBSTITUTED CYCLOPROPENE DERIVATIVES

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Abstract—According to MNDO calculated heats of formation for various 3-substituted cyclopropenes the π-acceptor methoxycarbonyl as well as the π-donor group phenyl both prefer a non-bisected orientation with respect to the three-membered ring. Temperature dependent NMR chemical shifts seem to confirm this behaviour for the free molecules. In the crystalline state, however, 1,2,3-triphenylcyclopropene (**3e**) and 3-isopropyl-1,2,3-triphenylcyclopropene (**3f**) both adopt a conformation with a bisected orientation of the 3-phenyl groups.

The rotational isomerism of several π-acceptor and π-donor substituted cyclopropanes has been studied by a variety of methods. Thus it has been established, that cyclopropyl carbonyl compounds[1-3] as well as cyclopropyl carbinyl cations[4] strictly prefer the so-called bisected conformation with its possibility for maximum interaction between the Walsh-e_A-orbital of the cyclopropyl group and the π- or p-orbital, respectively.[5] In vinylcyclopropane[6] and phenylcyclopropane[7-11] the preferences for the bisected conformations are less pronounced with energy differences to the less favourable conformers of only 1.1 kcal/mol[6] and 1.4 kcal/mol,[7] respectively. Surprisingly, nothing is known so far about the conformational behaviour of 3-substituted cyclopropenes except for a theoretical[12a] and a photoelectron spectroscopic[12b] study of 3,3'-bicyclopropenyl. In view of the apparent analogies and yet some distinct differences to be expected we have started to investigate a series of 3-phenyl-, 3-vinyl- and 3-carbomethoxy-cyclopropenes by appropriate methods. This is a report on our first results obtained by semiempirical MO calculations, ^{1}H-NMR measurements and an X-ray structure analysis.

Three types of orbital interactions may be relevant in determining any conformational preferences of cyclopropenes with π-acceptor and π-donor substituents at the 3-position.

Firstly the cyclopropene ring bonding can be described with the same set of σ- and e-Walsh-orbitals as those for cyclopropane[13] except that their energies are slightly higher.[14] This generally leads to a stronger interaction with a π-substituent as it is expressed by the experimental observation, that a cyclopropenyl group is a more effective electron donor to electron deficient centres than a cyclopropyl group.[15,16] The interaction of a π-substituent, e.g. a phenyl group, with the cyclopropene Walsh-e_A-orbital is at its maximum in the bisected ($\phi = 0°$) and non-existent in the perpendicular ($\phi = 90°$) conformation (see Fig. 1). This effect would therefore favour a bisected conformer for both classes of substituents. Due to this interaction any π-acceptor would cause a distal bond shortening and a lengthening of the vicinal bonds; π-donors would act accordingly. From an analysis of the structural parameters of 34 cyclopropene derivatives Allen has established some evidence that this type of substituent effect on bond lengths does indeed occur,[17] and this in turn seems to indicate the importance of the Walsh-e_A-π-interaction.

Secondly the π-orbital of the cyclopropene C=C double bond can interact through its CH_2-group component of appropriate symmetry with a substituent's π-orbital. This interaction is at its maximum with a perpendicular orientation of the substituent and it would accordingly favour a non-bisected conformer (Fig. 2), if this interaction were predominant, any π-acceptor would cause a distal bond lengthening and a vicinal bond shortening. Viewed from a different standpoint this electron withdrawal would induce some cyclopropenium ion character in the ring. As far as the bond length data[17] are significant, this effect appears to be of minor importance.

Thirdly one has to take into account the possibility for direct through-space interaction between the π-orbital of the cyclopropene double bond and a π-centre at C-1'. This interaction is of the homoallyl type as

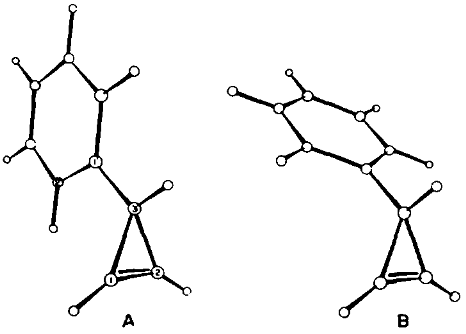
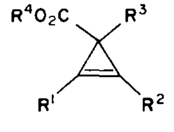


Fig. 1. Walsh-e_A-π-orbital interactions in (A) bisected (synplanar, $\phi = 0°$) and (B) perpendicular ($\phi = 90°$) 3-phenylcyclopropene (**3a**). ϕ is the dihedral angle between the plane of the phenyl group and the plane C-1'/C-3/3-H.

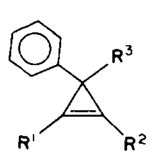
observed in 7-norbornenyl and 7-norbornadienyl cations.[18] It is at a maximum for a perpendicular orientation of the substituent's π-orbital with respect to the cyclopropene π-orbital, i.e. in the perpendicular conformation of, e.g. a 3-phenylcyclopropene (Fig. 3). Again this type of interaction would favour a non-bisected conformer. Through it a π-acceptor would exert a distal bond lengthening and a vicinal bond shortening effect (see above).

1



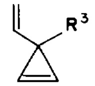
2

(a) $R^1, R^2, R^3 = H; R^4 = Me$
(b) $R^1, R^2 = H; R^3, R^4 = Me$
(c) $R^1, R^2, R^4 = Me; R^2 = H$
(d) $R^1, R^2 = Me; R^4 = Et; R^3 = H$
(e) $R^1, R^2 = Ph; R^4 = Me; R^3 = H$

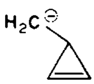


3

(a) $R^1, R^2, R^3 = H$
(b) $R^1, R^2 = H; R^3 = Me$
(c) $R^1, R^2 = H; R^3 = i\text{-}Pr$
(d) $R^1, R^2 = Me; R^3 = H$
(e) $R^1, R^2 = Ph; R^3 = H$
(f) $R^1, R^2 = Ph; R^3 = i\text{-}Pr$



4 (a) $R^3 = H$
(b) $R^3 = Me$



5

SEMIEMPIRICAL MO CALCULATIONS

Although the MNDO method[19] apparently overestimates strain energies of small ring compounds and therefore yields enthalpies of formation in poor agreement with their experimental values,[20] such calculations appeared to be useful for the series of cyclopropene derivatives **1**–**5** as a means of sorting out substituent and conformational effects on a relative scale.

In all cases, except for the carbocation **1**[21] and the carbanion **5**, the calculated enthalpies of formation (see Table 1) indicate a slight to significant favorization of the non-bisected conformations. The enthalpy difference is only marginal for the 3-methoxycarbonyl derivatives **2**, certainly too small to merit any rationalization. But for the 3-phenyl- **3** and 3-vinyl-substituted cyclopropenes **4** the $\Delta\Delta H_f = \Delta H_f$ (90°)

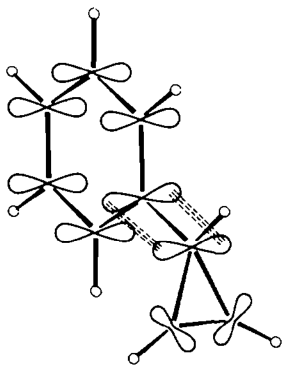


Fig. 2. Through bond interaction of π- and Walsh-orbitals in **3a**.

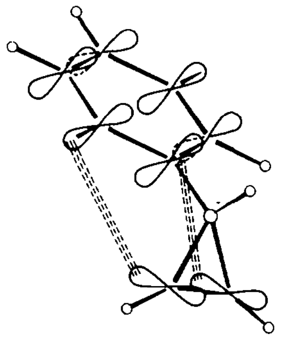


Fig. 3. Through space interaction of π-orbitals in **3a**.

Table 1. Enthalpies of formation (ΔH_f° in kcal/mol) calculated by the MNDO method for cyclopropene derivatives 1–5 in bisected and perpendicular conformations

	ΔH_f° (kcal/mol) Dihedral angle				ΔH_f° (kcal/mol) Dihedral angle		
Comp.	$\phi = 0°$	$\phi = 90°$	$\phi = 180°$	Comp.	$\phi = 0°$	$\phi = 90°$	$\phi = 180°$
1†	279.5	293.9	—	**3b**	94.7	89.4	—
2a	−13.1	−13.4	−13.0	**3c**	99.4	90.6	—
2b	−15.8	−17.9	−16.3	**3d**	66.5	65.5	—
2c	−41.5	−41.7	−41.3	**4a**	85.7	85.1	85.3
3a	95.0	93.6	—	**4b**	82.1	80.5	82.6
				5†	101.1	106.7	—

† Planar configurations resulted for the carbenium ion and carbanion centres of **1** and **5**, respectively.

$-\Delta H_f$ (0/180°) was found between 0.8 and 8.8 kcal/mol.

The bulkier the second substituent in the 3-position, the higher is the $\Delta\Delta H_f$ in favour of the perpendicular conformation ($\phi = 90°$), with a difference of 5.3 kcal/mol for the methyl **3b** and 8.8 kcal/mol for the isopropyl derivative **3c**. This finding may indicate that non-bonded interactions are overestimated in all the MNDO calculated heats of formation (see below).

^{1}H-NMR MEASUREMENTS

Closs and Klinger[7] determined the temperature dependence of the chemical shift difference between *ortho*- and *meta*-protons in *p*-deuteriophenylcyclopropane and concluded that the bisected ($\phi = 0°$) conformer is energetically favoured over a non-bisected one by 1.4 kcal/mol. On the basis of a nearly complete analysis of the ^{1}H-NMR spectrum of phenylcyclopropane Parr and Schaefer[10] essentially supported this conclusion. In analogy to these studies we have attempted to determine the conformational preferences for the cyclopropene-3-carboxylates **2d** and **2e** as well as the 3-phenylcyclopropanes **3d** and **3e**. If there are temperature dependent equilibria between bisected conformers such as A-**2**(**3**) (Fig. 4) and non-bisected ones such as B-**2**(**3**) or any other with dihedral angles $0° < \phi < 180°$, then the observed 3-H chemical shift should show a temperature dependence, because in A-**2**(**3**) the 3-proton is in the deshielding and in B-**2**(**3**) it is in the shielding region of the diamagnetically anisotropic carbonyl or phenyl group, respectively.

The measurements were made on a 270 MHz NMR instrument with extremely high field stability. The temperature dependence of the chloroform signal was monitored with respect to the instrumental standard.

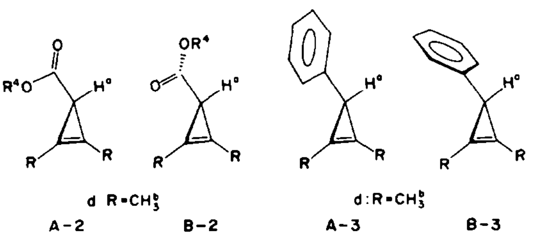


Fig. 4. Different electronic environments of 3-H (H^a) in bisected (A) and non-bisected (B) conformers of cyclopropenes **2** and **3**.

For **2d** and **3d** the temperature independent chemical shift difference between the CH_3- and the $CHCl_3$-signal served as an additional cross-check. Although all the observed changes lack the desirable uniformity (Table 2), they firmly establish a significant high-field shift of the 3-H (H^a in Fig. 4) signal with decreasing temperature at least for **2d** and **3d**. The same trend is visable for **2e** and **3e**, though it is less apparent (Table 2).

This observation might be taken as a qualitative account for an increasing population of the non-bisected conformation at lower temperature, i.e. the non-bisected conformer should be of lower free energy. This conclusion would hold only if there were no other reasons for the temperature dependence of these chemical shift differences. It—maybe fortuitously—agrees with the results obtained from MNDO calculations (see above).

X-RAY STRUCTURE ANALYSES OF **3e** AND **3f**

Compound **3e** formed monoclinic crystals of space group I_2/C with eight molecules in the unit cell of

Table 2. Temperature dependence of the 3-H (H^a in Fig. 4) chemical shifts for cyclopropenes **2d**, **e** and **3d**, **e**. $\Delta\delta = \delta_H - \delta_{HCCl_3}$ in Hertz at 270 MHz, with δ_{HCCl_3} determined at each temperature. $\Delta\delta_{H^b}$ in parentheses for comparison

Comp.	**2d**		**2e**	**3d**		**3e**
Temp [K]	$\Delta\delta_{H^a}$	($\Delta\delta_{H^b}$)	$\Delta\delta_{H^a}$	$\Delta\delta_{H^a}$	($\Delta\delta_{H^b}$)	$\Delta\delta_{H^a}$
293	−1423.1	(−1412.1)	−1194.0	−1311.3	(−1403.1)	
287						−1080.7
273	−1425.0	(−1412.3)	−1194.1	−1312.8	(−1403.4)	
272						−1078.2
263	−1425.7	(−1412.6)				
253	−1426.2	(−1411.9)	−1194.3	−1313.9	(−1404.2)	−1082.6
243	−1426.4	(−1411.5)				
233	−1428.1	(−1411.9)		−1315.2	(−1404.2)	−1081.1
223	−1427.9	(−1411.2)	−1194.6			
213	−1429.9	(−1411.7)		−1317.8	(−1406.4)	−1083.1
203	−1429.8	(−1411.03)				
193			−1196.8	−1319.6	(−1406.9)	
183						−1085.4

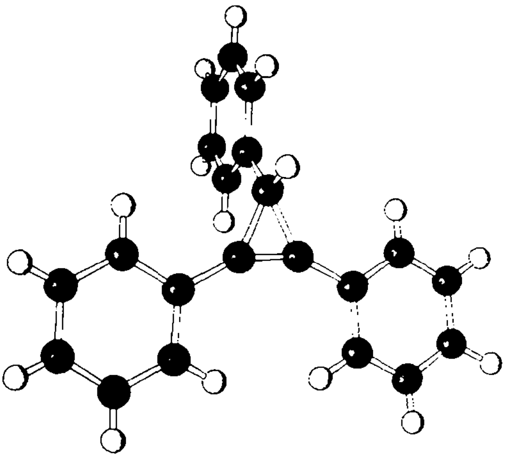


Fig. 5. SCHAKAL-plot of the crystal molecular structure of 1,2,3-triphenylcyclopropene (**3e**).

dimensions $a = 15.127$, $b = 8.119$, $c = 24.586$ Å, $\beta = 93.61°$. A total of 1952 reflections out to $2\theta_{max} = 55°$ were recorded. Crystals of **3f** were monoclinic, space group C2 with four molecules in the unit cell of dimensions $a = 15.799$, $b = 11.767$, $c = 9.708$ Å, $\beta = 92.06°$. In total 1688 reflections out to $2\theta_{max} = 55°$ were recorded. The structure problems were solved using the SHEL-X 76 program system[22] and refined to $R = 7.1\%$ ($R_w = 4.0\%$) and $R = 5.0\%$ ($R_w = 3.5\%$), respectively.[23]

In the crystals both 1,2,3-triphenylcyclopropene (**3e**) and 3-isopropyl-1,2,3-triphenylcyclopropene (**3f**) adopt geometries with bisected conformations of the 3-phenyl groups (dihedral angles with the plane $C^1C^2C^3$ of 89.8° and 86.6°, respectively) and completely coplanar arrangements of the 1- and 3-phenyl groups with the three-membered rings (Figs 5 and 6).

All the endocyclic and exocyclic bond lengths of the cyclopropene rings in **3e** and **3f** (Tables 3 and 4) are essentially the same as those found for dicarbonyl-(η^5-cyclopentadienyl)-(1,2,3 - triphenylcyclopropen - 1 - yl)iron.[24]

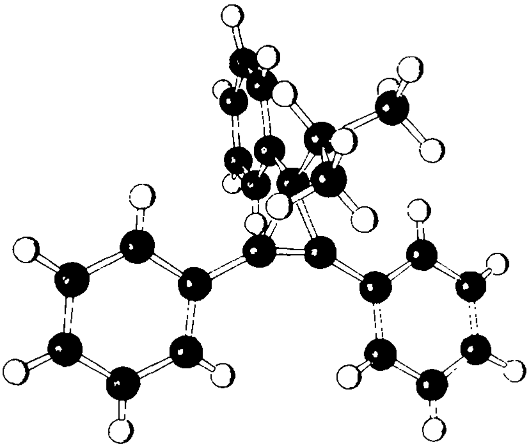


Fig. 6. SCHAKAL-plot of the crystal molecular structure of 3-isopropyl-1,2,3-triphenylcyclopropene (**3f**).

Table 3. Crystal structure parameters of 1,2,3-triphenylcyclopropene (**3e**)

Bond	pm	Angle	(°)
C^1—C^2	129.3(4)	$\sphericalangle C^2C^1C^3$	65.0(2)
C^1—C^3	151.3(3)	$\sphericalangle C^3C^2C^1$	64.6(2)
C^2—C^3	151.8(3)	$\sphericalangle C^1C^3C^2$	50.5(2)
C^1—C^{11}	142.2(4)	$\sphericalangle C^2C^1C^{11}$	153.4(2)
C^2—C^{21}	144.3(3)	$\sphericalangle C^1C^2C^{21}$	152.6(2)
C^3—C^{31}	147.0(4)	$\sphericalangle C^1C^3C^{31}$	121.7(2)

Average C—C (phenyl-1) 137.4(4).
Average C—C (phenyl-2) 137.7(4).
Average C—C (phenyl-3) 137.5(4).
Dihedral angles: $\sphericalangle C^{11}, C^{12}, C^{13}, C^{14}, C^{15}, C^{16}/C^1C^2C^3$ 1.1°; $\sphericalangle C^{21}, C^{22}, C^{23}, C^{24}, C^{25}, C^{26}/C^2C^1C^3$ 5.4°; $\sphericalangle C^{31}, C^{32}, C^{33}, C^{34}, C^{35}, C^{36}/C^3C^1C^2$ 89.8°.

In addition, the endocyclic C═C bond lengths in **3e** and **3f** do not significantly differ from those in the parent cyclopropene;[25] apparently the electronic effect of the 3-phenyl substituent is too weak to induce any observable changes in the distal and vicinal bond lengths. This is in accord with conclusions drawn from a large number of known cyclopropene structures.[17]

DISCUSSION

In both 3-phenylcyclopropenes **3e** and **3f** the 3-phenyl group essentially prefers the bisected orientation at least in the crystalline state. This contrasts the results of MNDO calculations which yield higher heats of formations for the bisected conformers and thereby predict a preference of this orientation in the free molecules. Even the bulky isopropyl substituent in **3f** only rotates the 3-phenyl group by ~3° out of this orientation which should be favoured by a maximum overlap between phenyl-π and cyclopropene-Walsh-e_A orbitals. Apparently crystal packing effects play an important role in view of an extremely short $H^{36} \cdots H^{37}$ distance of only 195 pm, which should lead to considerable non-bonded repulsion. Only with an even bulkier substituent in the 3-position as in dicarbonyl-(η^5 - cyclopentadienyl) - (1,2,3 - triphenylcyclopropen - 1-yl)iron,[24] is the 3-phenyl group forced out of the bisected conformation.

Although stable conformations observed in crystals

Table 4. Crystal structure parameters of 3-isopropyl-1,2,3-triphenylcyclopropene (**3f**)

Bond	pm	Angle	(°)
C^1—C^2	129.8(5)	$\sphericalangle C^2C^1C^3$	64.5(3)
C^1—C^3	151.8(5)	$\sphericalangle C^3C^2C^1$	64.8(3)
C^2—C^3	151.4(7)	$\sphericalangle C^1C^3C^2$	50.7(2)
C^1—C^{11}	144.8(5)	$\sphericalangle C^2C^1C^{11}$	151.5(4)
C^2—C^{21}	143.7(7)	$\sphericalangle C^1C^2C^{21}$	151.2(4)
C^3—C^{31}	150.9(7)	$\sphericalangle C^1C^3C^{31}$	116.1(3)

Average C—C (phenyl-1) 137.3(7).
Average C—C (phenyl-2) 137.5(7).
Average C—C (phenyl-3) 137.5(8).
Dihedral angles: $\sphericalangle C^{11}, C^{12}, C^{13}, C^{14}, C^{15}, C^{16}/C^1C^2C^3$ 10.2°; $\sphericalangle C^{21}, C^{22}, C^{23}, C^{24}, C^{25}, C^{26}/C^2C^1C^3$ 10.1°; $\sphericalangle C^{31}, C^{32}, C^{33}, C^{34}, C^{35}, C^{36}/C^3C^1C^2$ 86.6°.

may in certain instances be determined by crystal packing effects, it is unlikely that the free molecules of **3e** and **3f** will exhibit a different conformational preference in spite of the conflicting conclusions drawn from the observed chemical shift changes in the temperature dependent NMR spectra. Even the agreement of this result with the MNDO calculations may be fortuitous, since the MNDO method is known to slightly overestimate non-bonded interactions. The current experimental evidence cannot unequivocally be interpreted, the remaining discrepancy may, however, be resolved by a gas phase electron diffraction study on one of the 3-phenylcyclopropenes.[26]

EXPERIMENTAL

The calculations were performed on a TR 440 computer at the University of Hamburg Computing Centre using an MNDO[19] program version kindly supplied by Prof. P. von R. Schleyer, University of Erlangen. ^{1}H-NMR measurements were made on a BRUKER WH 270 with a variable temperature probe using 10% solns of the compounds in $CDCl_3$. Temp dependent chemical shifts were recorded with reference to the instrumental frequency generator standard. Routine ^{1}H-NMR spectra were recorded on T-60 spectrometer (60 MHz) for 20% solutions of substances in $CDCl_3$ with TMS as an internal standard. An automated four circle diffractometer (SYNTEX $P2_1$) was used for the X-ray single crystal structure analysis of **3e**. A total of 1952 reflections out to $2\theta_{max} = 55°$ were recorded, the structural problem was refined to $R = 7.1\%$ ($R_w = 4.0\%$, $W = 1/\sigma$) yielding the parameters listed in Tables 3 and 4.[23] IR-spectra of neat liquids were recorded on a Beckman AccuLab 4 instrument. High resolution mass spectra were measured on a Hewlett-Packard HP 5711 GC–MS system.

Ethyl 1,2-dimethylcyclopropene-3-carboxylate (**2d**). The compound was prepared according to the procedure of Vidal *et al.*[27]

Methyl 1,2-diphenylcyclopropene-3-carboxylate (**2e**). A sample was prepared according to the procedure of D'yakonov *et al.*[28]

1,2-Dimethyl-3-phenylcyclopropene (**3d**). The procedure of Olofson and Dougherty[29] has been adopted with some modifications. In a 500 ml round-bottomed 3-necked flask fitted with a magnetic stirrer dry ice condenser, dropping funnel and Ar inlet was placed 27 g (0.5 mol) of 2-butyne, diluted with an equal amount of dry ether and 6.3 g (0.05 mol) of freshly distilled benzylchloride. A soln of lithium 2,2,6,6-tetramethylpiperidide (LiTMP) was prepared just before use in the addition funnel by treatment of an ethereal soln of 13.8 g (0.1 mol) of 2,2,6,6-tetramethylpiperidine with 52.6 ml 1.9 M n-BuLi soln in n-hexane. The LiTMP soln was added within 0.5 h to the stirred soln of benzylchloride and butyne-2 and the mixture was refluxed for another 5 h. After that period of time a sample was taken from the reaction mixture and examined by ^{1}H-NMR spectroscopy to prove the absence of benzylchloride with signals in the region near 4.3 ppm. Then an equal volume of cold water was added and the organic layer was washed with 30 ml each of 10% HCl, water, sat NaCl soln and dried over $MgSO_4$. After evaporation of the solvents 6.5 g of crude product was obtained. After column chromatography on 300 g silica gel L40/100 mesh 4 g (56%) of cyclopropene **3d** was eluted with n-hexane. ^{1}H-NMR (270 MHz, $CDCl_3$): 1.97 (s, 6H, $2CH_3$), 2.37 (s, 1H, H), 7.07 (m, 5H, C_6H_5). IR film: 1895 (νC=C), 1613, 1502 cm^{-1}. GC–MS (70 eV): 144 (M^+, 10.1%), 129 ($M^+ - CH_3$, 100%). $C_{11}H_{12}$ calc 144.09390, found 144.09389 (MS). A pure sample was obtained by preparative thin layer chromatography on silica gel L40/100 mesh with n-hexane ($R_f = 0.4$).

1,2,3-Triphenylcyclopropene (**3e**). Prepared from triphenylcyclopropenium bromide according to the procedure of Breslow and Dowd.[30]

3-Isopropyl-1,2,3-triphenylcyclopropene (**3f**). Prepared from triphenylcyclopropenium bromide by reaction with isopropyl magnesium bromide,[30] 79% yield, twice recrystallized from n-hexane, m.p. 102.5–103.5°. ^{1}H-NMR (60 MHz, CCl_4): 0.98 (d, 6H, CH_3), 3.10 (septet, 1H, C—H), 7.60 (m, 15H, C_6H_5). IR (CCl_4): 3095, 3085, 3020, 2980, 2890, 2300, 1820, 1805, 1720, 1580, 1550, 1450, 1385, 1360, 1250, 1215, 1100, 1060, 1000, 975 cm^{-1}. (Found: C, 92.52; H, 6.62; C, 92.69; H, 7.36. Calc for $C_{24}H_{22}$ (310.17): C, 92.86; H, 7.14%.) The crystal for X-ray analysis was grown from a diluted n-hexane soln.

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