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Contribution to the knowledge of photochemistry of *o*-carbonylstyrenes

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Abstract

The photochemistry of substituted o-carbonylstyrenes was investigated. Depending on substitution two different reaction pathways were observed, leading either to cyclization products or to dimer formations. © 1997 Elsevier Science S.A.

Keywords: *o*-Carbonylstyrenes; 2-Carbonylstyrenes

1. Introduction

The results reported on the photochemistry of substituted 2-carbonylstyrenes are contradictory. Huffman and Ullman [1] and Chu and Tschir [2] found that an electrocyclic reaction was dominant, leading to isochromane derivatives, whereas Kessar and Mankotia [3] claimed that a photochemical cycloaddition of a carbonyl moiety to an intermediate formed by a cross $[\pi_a^2+\pi_s^4]$ cycloaddition occurred. We became interested in the substituent effects and the conformation necessary for these reactions and investigated the photochemistry of the substituted 2-carbonylstyrenes **1a–1e**.

2. Experimental section

2.1. Syntheses

2.1.1. Compounds 1a–1d

These compounds were synthesized according to a Bischler–Napieralski synthesis [4] with polyphosphoric acid (PPA), followed by conversion to the carbonylstyrenes by reaction with dimethyl sulphate. Product **1b** is a by-product of **1a** in the reaction with dimethyl sulphate. The substances were separated by column chromatography. In the case of **1a** and **1d** purification was achieved by distillation.

2.1.2. General procedure

The amides were obtained by heating a mixture of 1 mol of phenylethylamine and 1 mol of the corresponding acid at 150 °C for 2 h with stirring. The amides were obtained in 80–95% yields. After cooling to room temperature the solid product was mixed with 200 ml of PPA and heated at 165 °C, with efficient stirring, for 3 h. The PPA phase was dissolved in a mixture of 600 ml ice and water. Solid sodium hydroxide was added until the reaction mixture was alkaline. The reaction mixture was extracted four times with 100 ml portions of diethyl ether. The organic phase was dried over sodium sulphate. The ether was removed in vacuo and the product was distilled under reduced pressure at 0.01 Torr (boiling ranges and yields of the substituted dihydroisoquinolines: R = H: 45–55 °C, 30%; R = CH_3: 75–85 °C, 50%; R = C_6H_5: 110–115 °C, 30%). Amounts of 0.25 mol of the substituted dihydroisoquinolines were mixed with 600 ml water and 300 g solid sodium hydroxide. 75 ml distilled dimethyl sulphate were added slowly to the mixture at a temperature of 70 °C with efficient stirring. The reaction mixture was stirred for a further 2 h at a temperature of 85 °C. After cooling to room temperature, the solution was extracted three times with 150 ml portions of diethyl ether. The organic phase was washed with water and sodium carbonate and dried over sodium sulphate. The ether was removed in vacuo and the products were distilled under reduced pressure at 0.03 Torr (boiling ranges and yields of the substituted 2-carbonylstilbenes: R = H: 40–45 °C, 17%; mixture of R = CH_3 and R = C_2H_5: 42–50 °C, 23%; R = C_6H_5: 107–110 °C, 57%). In the case of 1-methyl-2,3-dihydroisoquinoline, two cleavage products **1b**

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and **1c** were obtained. They were separated by column chromatography on silica gel with heptane/diisopropylether, 85:15 v/v. Product ratio **1b/1c** = 3:2).

2.1.3. 2,2'-Divinylbenzophenone 1e

This compound was formed by ozonolysis at a temperature of −70 °C of commercially available dibenzosuberenone, followed by a Wittig reaction [5]. The substance was separated from the tris-vinyl product by column chromatography.

2.1.3.1. Procedure

Dibenzosuberenone (5 g) was dissolved in 60 ml chloroform and cooled to −70 °C. Ozonolysis was performed for 30 min. Thereafter the reaction mixture was stirred with 20 g sodium iodide in 20 ml acetic acid for 1 h. The solution was extracted twice with chloroform. The organic phase was washed with water and a solution of sodium carbonate to neutralize it and was dried over sodium sulphate. The solvent was removed in vacuo and the residue was purified by column chromatography on silica gel with heptane/diethyl ether, 75:25 v/v. Colourless crystals with a melting point of 120 °C were obtained in a yield of 43%.

The dialdehyde (2 g) was dissolved in 150 ml of dry dimethoxyethane and added to a stirred solution of 6.5 g triphenylmethylphosphonium iodide and 2 g of potassium *tert.*- butanolate in 200 ml dry diethyl ether. After stirring overnight the solution was filtered and concentrated in vacuo. The solid residue was removed by filtration and the solution was washed with a mixture of methyl alcohol and water (1:1 v/v) and dried over sodium sulphate. The solvent was removed in vacuo and the residue was purified by column chromatography on silica gel with heptane/diethylether, 90:10 v/v. The 2,2'-divinylbenzophenone was eluted as the second fraction. Colourless crystals were obtained in 14% yield (melting point 156 °C).

2.2. Irradiations

Preparative irradiations were run using 10^{-3} mol l^{-1} solutions of the starting materials in degassed benzene in a Rayonet Photochemical Reactor (Southern New England Ultraviolet Company) at a wavelength of 300 nm (**1a–1c**) and 360 nm (**1d** and **1e**) for 3 h under a N_2 atmosphere at room temperature. The solvent was removed in vacuo and the residue was fractionated by preparative thin layer chromatography with heptane/diisopropyl ether, 85:15 v/v, in the case of **5a**. In the case of **5b** and **5c** purification was performed by preparative HPLC with heptane/diisopropyl ether, 75:25 v/v, plus 1% acetonitrile. **5d** and **7d** were separated by preparative HPLC with heptane/diisopropyl ether, 85:15 v/v, plus 1% acetonitrile. **7e** and **8e** were separated by column chromatography on silica gel with heptane/diethyl ether, 90:10 v/v.

2.3. Trapping reactions

Preparative irradiations were run using 10^{-3} mol l^{-1} solutions of the starting materials in dimethyl acetylenedicarboxylate in a Rayonet Photochemical Reactor (Southern New England Ultraviolet Company) at a wavelength of 300 nm (**1b**) and 360 nm (**1e**) for 3 h under a N_2 atmosphere by room temperature. The product was fractionated by preparative thin layer chromatography with heptane/diisopropyl ether, 80:20 v/v.

In the TCNE trapping experiment, a solution of 10^{-3} mol l^{-1} TCNE and 10^{-3} mol l^{-1} **1e** in degassed benzene was irradiated at a wavelength of 360 nm for 6 h under a N_2 atmosphere at room temperature. The solvent was removed in vacuo and the residue was fractionated by preparative thin layer chromatography with neat diisopropyl ether.

2.4. Quantum yields

The quantum yields were measured with an electronic integrating actinometer as described by Amrein and Gloor [6]. Calibration was carried out using potassium ferrioxalate actinometry. The product formation was monitored by analytical HPLC with methanol/water, 77:23 v/v. Solutions were purged with N_2 [7].

2.5. AM1 calculations

The AM1 calculations to obtain the heats of formation of the dimers **4a** and **5a** were performed with the program Hyper Chem 3.0 (Hypercube, Inc. and Autodesk, Inc.) using an single point semi-empirical AM1 method after a geometry opimization with the Polak–Ribiere algorithm.

2.6. Spectral data

The connectivities were substantiated by INADEQUATE and HMBC techniques, and were in accordance with the structures obtained by X-ray analysis.

The NMR spectra were run in $CDCl_3$ and the IR spectra in CCl_4. For the IR and mass spectra only characteristic signals will be given. In a few cases the signals overlap in the aromatic region.

2.7. Instrumental analysis

NMR: Bruker DRX-400 (400 MHz/94.4 kG, FT).

MS: Varian CH-5 (70 eV); high-resolution MS: VG Autospec (70 eV).

IR: Perkin-Elmer 881.

X-ray: Siemens Diffraktometer P4.

Melting point: Apparatus of Büchi and Flawil. All melting points are corrected.

HPLC

Analytical: injector: Waters-UK6; pump: LDC Laboratory Data Control (Milton Roy); detection: LDC UV-detector

monitor III (Milton Roy); column: 125×4.6 mm filled with Shandon Hypersil ODS 3 μm.

Preparative: injector: Reodyne 7125; pump: Knauer 64; detection: differential refractometer monitor III (Milton Roy); column: 150×15.5 mm filled with Shandon Hypersil ODS 10 μm.

Ozonolysis: Fischer ozone producer (Labor- & Verfahrenstechnik).

Thin layer chromatography: PSC plates (20×20 cm, layer thickness 2 mm), Merck with fluorescence indicator $F_{254+366}$.

Column chromatography: Run on Machery-Nagel silica gel 60–100 mm.

3. Results

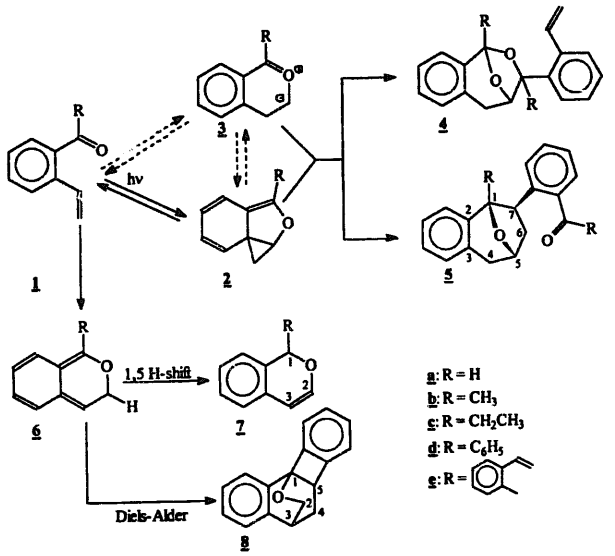
3.1. Syntheses of starting materials

Compounds **1a–1d** were obtained by Bischler–Napieralski reaction followed by conversion with dimethyl sulphate, leading to the desired starting materials. Compound **1e** was obtained by ozonolysis of commercially available dibenzosuberenone followed by a Wittig reaction. Details of the syntheses are given in Section 2, above.

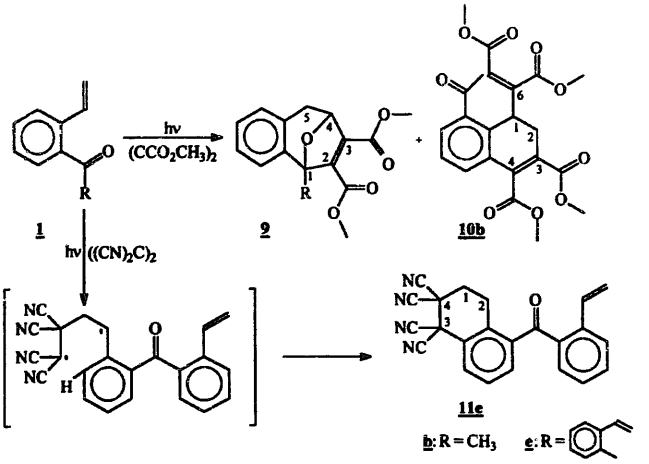
3.2. Irradiation of carbonylstyrenes

Kessar and Mankotia recently reported on the photochemistry of *o*-vinylbenzaldehyde **1a** [3]. They claimed that the dimer **4a** is formed from an intermediate spiro triene **2** by cycloaddition to the carbonyl group of a second molecule of the starting material (Scheme 1).

As it is known that carbonyl ylids are apt to add to alkenes or carbonyl compounds in a 1,3-dipolar cycloaddition reaction [8], either **2** or **3** might be an intermediate along the reaction pathway.



Scheme 1. Photochemistry of the investigated compounds.



Scheme 2. Trapping reactions.

In this work the irradiation of the compounds **1a**, **1b** and **1c** afforded the dimers **5a**, **5b** and **5c** as the only identifiable products apart from polymers by cycloaddition of the vinyl moiety of a second molecule of starting material **1** to the intermediate **2** or **3**. In contrast to the findings of Kessar and Mankotia, we were not able to isolate compound **4a**. Preparative irradiations were performed using 10-3 mol l-1 solutions of starting material in benzene. The product yield of 5a in the reaction mixture was determined by 1H NMR to be about 1%. The product yields were 5b 14%, 5c 5%, and 5d 2% after chromatographic isolation. Details are given in the experimental section

Irradiation of compound **1d** afforded a monocyclization product **7d** in addition to the dimer **5d**. In contrast, irradiation of **1e** led to a monocyclization product **7e** and a tricyclic product **8e**. No product of structure **5** was obtained.

In order to prove that **2** and **3** are intermediates along the reaction pathway, we performed trapping reactions with dimethyl acetylenedicarboxylate and tetracyanoethylene (TCNE).

Whereas trapping with dimethyl acetylenedicarboxylate of **1b** and **1e** led to **9b** and **9e** as the expected photoproducts, the trapping experiment with TCNE surprisingly afforded only **11e**. In the trapping of **1b** with dimethyl acetylenedicarboxylate, a second product **10b** was formed by double addition of dimethyl acetylenedicarboxylate (Scheme 2).

3.3. Quantum yields

The quantum yields of product formation were obtained for compound **1b** ($\phi = 0.0047 \pm 0.0002$ at a conversion of 0.145%), **1c** ($\phi = 0.0038 \pm 0.0002$ at a conversion of 0.089%) and **1d** ($\phi = 0.0043 \pm 0.0002$ at a conversion of 0.12%). For the conversion of **1a** to **5a** no quantum yield could be obtained because the amount of product was too low for detection by HPLC.

4. Discussion

The cycloaddition of C=C double bonds to a carbonyl ylid was demonstrated by Ullman and Milks [9](b). They

examined the tautomerization between 1,3-diphenyl-2-benzopyrilium-4-oxide and 2,3-diphenylindenone oxide. In accordance with these results [9] we observed the cycloaddition of the vinyl moiety of a second molecule to the intermediate in the case of **1a–1d**, possibly via a 1,3-dipole **3**, leading to **5a–5d**. The regiospecifity of the addition of the vinyl group could be explained by polarization by placing a positive charge on the carbon atom of the carbonyl group and on the terminal methylene group of the vinyl moiety.

Even in the case of 2-vinylbenzaldehyde **1a**, as we noted above, we did not observe the cycloaddition of the carbonyl moiety of a second molecule of starting material to the intermediate. To our knowledge no clear-cut example of a cycloaddition of a carbonyl group to a carbonyl ylid has been reported.

Kagan et al. claimed that irradiation of 2-methyl-3-phenylglycidate led to a carbonyl ylid which reacted further to a carbene and an aldehyde [10]. No cycloaddition of a carbonyl compound to the carbonyl ylid was observed even in the presence of a tenfold excess of benzaldehyde. Another work substantiated these results [11].

As we can assume that the cycloaddition of a vinyl or a carbonyl group to the intermediate 1,3-dipole **3** is a ground state reaction, AM1 calculations were performed for the dimers **4a** and **5a**. We found that the acetal dimer **4a** needed a heat of formation of -28.27 kJ mol^{-1} whereas the dimer **5a** needed -97.63 kJ mol^{-1}. On the basis of the energy balance-sheet, formation of **5a** is favoured over the formation of **4a**.

Irradiation of **1d** afforded a monomeric product **7d** in addition to the dimer **5d**. We assumed that **7d** was formed by an electrocyclic ring closure of **1d** via the intermediate formation of an *ortho*-quinidimethane **6d** followed by a 1,5-H-shift. Trapping of **3b** formed by irradiation of **1b** with dimethyl acetylenedicarboxylate led to the expected cycloaddition product **9b**. **10b** as a side product was formed by a double addition of dimethyl acetylenedicarboxylate. Surprisingly, only a trapping product of intermediate **2e** was found in the case of the reaction of **1e** with dimethyl acetylenedicarboxylate. Trapping of **1e** with TCNE led only to a diradical addition product of TCNE to a vinyl moiety. Irradiation of **1e** without trapping reagent led to the photoproduct **8e** (and also **7e**) formed by intramolecular Diels–Alder reaction of the intermediate **6e** and the vinyl moiety of the second styrene.

These results imply an equilibrium between **1** and **2** and/or **3**. The bulky substituent R = styrene prevented a cycloaddition of **2e** or **3e** with a second molecule to **5e**, but did not prevent cycloaddition with the less space-consuming dimethyl acetylenedicarboxylate. Without trapping reagent the route from **1e** to **6e** was followed and products **7e** and **8e** were formed.

AM1 calculations on geometry-optimized structures of the starting materials **1a–1e** demonstrated that the favourable conformation for cyclization of **1** to **6** was reached only if large substituents were situated on the carbonyl group.

5. Summary

These results demonstrate that the substituents have a marked influence on the reaction pathway. Whereas the smaller groups R = H–, R = CH_3– and R = C_2H_5– showed only a minor effect, leading to the dimers **5a–5c**, the bulkier phenyl group led to the monocyclization product **7d** competing with **5d**. AM1 calculations and geometry optimizations supported this assumption. The quinoid intermediate **6**, forming photoproduct **7**, was proved by internal trapping, whereas external trapping with dimethyl acetylenedicarboxylate and tetracyanoethylene failed. External trapping with dimethyl acetylenedicarboxylate proved the existence of intermediate **2**.

The structures of the dimers and those of some trapping products could be elucidated by conventional spectral analyses, INADEQUATE ^{13}C-NMR and X-ray structural analyses.

In the case of **5d** two different types of crystals were obtained, which could be separated. X-ray analysis performed on the two species showed only a difference in the position of the phenyl group. Details are given in Section 2. The results of the X-ray structural analyses are given in Fig. 1.

6. Data obtained

6.1. 2-Vinylbenzaldehyde 1a

Compound **1a** was obtained as a colourless liquid. ^{1}H-NMR: 5.50 (dd, 1 H, vinylic CH_2), 5.65 (dd, 1 H, vinylic CH_2), 7.25 (dd, 1 H, vinylic CH), 7.30–7.85 (m, 4 H, aromatic), 10.25 (s, 1 H, aldehyde). ^{13}C-NMR: 119.81, 127.85, 128.33, 131.63, 133.78, 134.20, 192.80. IR: 3084, 3062, 1710. MS: 132 (M^+, base peak), 131, 104, 103, 78, 77, 51, 50, 39.

6.2. 2-Vinylacetophenone 1b

Compound **1b** was obtained as a colourless liquid. ^{1}H-NMR: 2.58 (s, 3 H, CH_3); 5.34 (dd, 1 H, vinylic CH_2), 5.63 (dd, 1 H, vinylic CH_2), 7.18 (dd, 1 H, vinylic CH), 7.28–7.66 (m, 4 H, aromatic). ^{13}C-NMR: 30.66, 116.89, 127.67, 127.77, 127.87, 131.78, 137.71, 137.92, 166.11, 202.24. IR: 3066; 3030, 2935; 1700, 1654. MS: 146 (M^+), 145, 131, 103 (base peak), 77, 51, 43.

6.3. 2-Vinylpropiophenone 1c

Compound **1c** was obtained as a colourless liquid. ^{1}H-NMR: 1.15 (t, 3 H, CH_3), 2.77 (q, 2 H, CH_2), 5.30 (d, 1 H, vinylic CH_2), 5.62 (dd, 1 H, vinylic CH_2), 7.08 (dd, 1 H, vinylic CH), 7.27–7.58 (m, 4 H, aromatic). ^{13}C-NMR: 8.65, 35.53, 116.78, 127.53, 127.65, 127.95, 131.26, 135.84, 137.39, 138.27, 205.80. IR: 3069, 3030, 2942, 1682, 1598. MS: 160 (M^+), 131 (base peak), 103, 77.

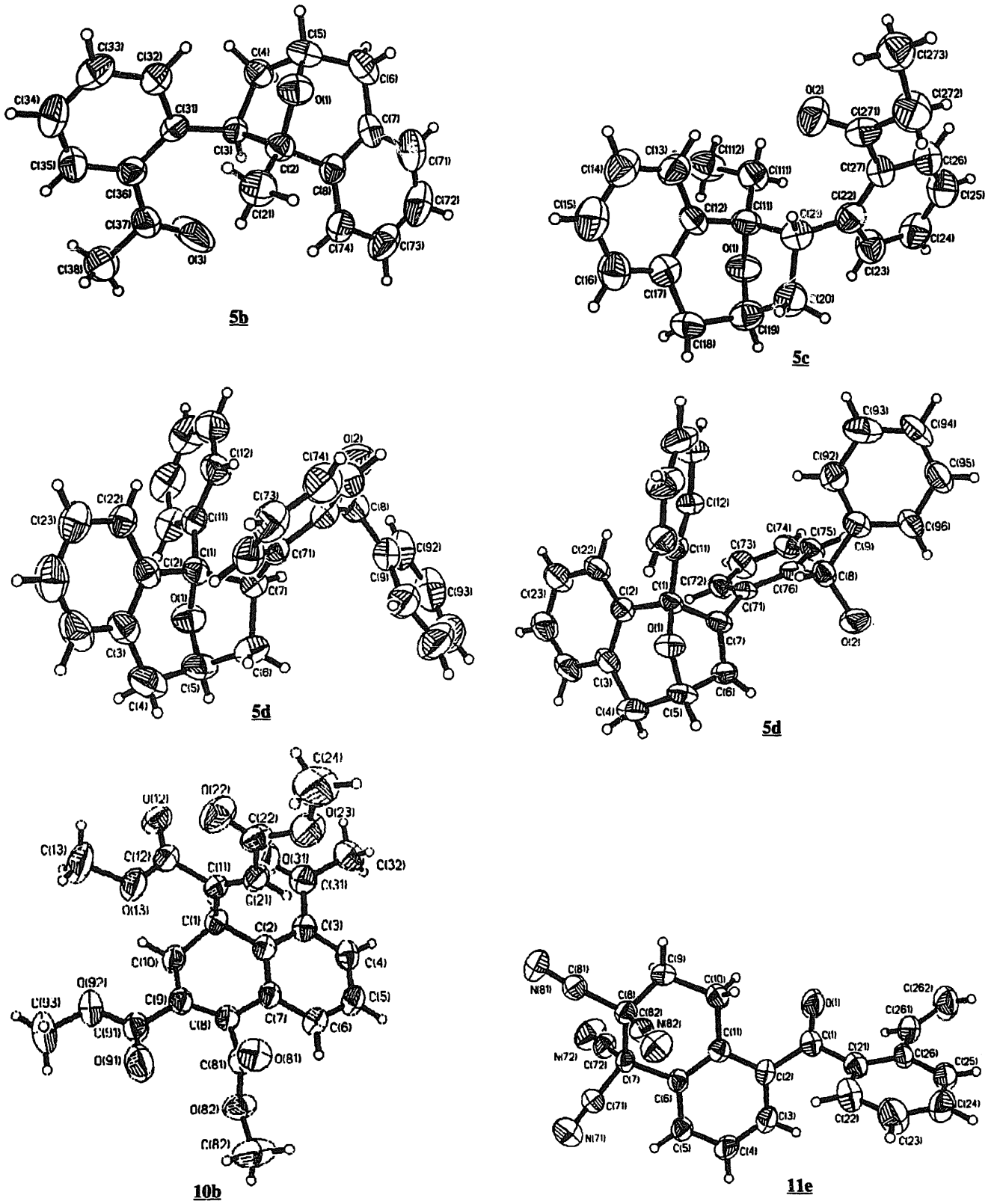


Fig. 1. ORTEP drawings of the conformers of **5b**, **5c**, **5d**, **10b** and **11e**.

6.4. 2-Vinylbenzophenone 1d

Compound **1d** was obtained as a colourless liquid. ^{1}H-NMR: 5.22 (dd, 1 H, vinylic CH_2), 5.75 (dd, 1 H, vinylic CH_2), 6.76 (dd, 1 H, vinylic CH), 7.32–7.79 (m, 9 H, aromatic). ^{13}C-NMR: 116.52, 116.76, 126.47, 128.03, 128.92, 129.33, 130.58, 131.00, 131.05, 134.84, 136.87, 138.35, 138.95, 197.92. IR: 3089, 3029, 1665, 1596, 1580. MS: 208 (M^+, base peak), 207, 179, 131, 105, 103, 77, 51.

6.5. 2,2'-Divinylbenzophenone ***1e***

Compound **1e** was obtained as a colourless liquid. ^{1}H-NMR: 5.24 (dd, 2 H, vinylic CH_2), 5.65 (dd, 2 H, vinylic CH_2), 7.02 (dd, 2 H, vinylic CH), 7.20–7.70 (m, 8 H, aromatic). ^{13}C-NMR: 116.64, 126.71, 127.12, 130.44, 131.43, 134.99, 137.90, 138.26, 199.85. IR: 3026, 2960, 1699, 1624, 1597. MS: 234 (M^+), 232, 219, 216, 215, 205, 191, 131, 103, 102, 91, 77 (base peak), 51.

6.6. (5α,6β,8α)-1-[2-(6,7,8,9-Tetrahydro-5,8-epoxy-5H-benzocyclohepten-6-yl)phenyl]benzaldehyde ***5a***

The dimer **5a** was obtained as a colourless liquid. ^{1}H-NMR: 2.30 (dt, 2 H, 6), 2.55 (t, 1 H, 4), 3.40 (dd, 1 H, 6), 4.47 (dd, 1 H, 7), 4.95 (s, 1 H, 1), 5.30 (s, 1 H, 5), 7.05–7.85 (m, 8 H, ArH), 10.20 (s, 1 H, aldehyde). ^{13}C-NMR: 36.43, 38.75, 49.50, 78.74, 83.00, 124.31, 124.99, 126.28, 127.59, 128.41, 129.67, 131.11, 131.52, 132.44, 134.72, 140.19, 145.68, 193.36. IR: 3074, 2959, 1707, 1601, 1113, 1056. MS: 264 (M^+), 246, 149, 145, 133, 132, 131, 118 (base peak), 117, 115, 104, 103, 78, 77, 51, 42, 39.

6.7. (5α,6β,8α)-1-[2-(6,7,8,9-Tetrahydro-5-methyl-5,8-epoxy-5H-benzocyclohepten-6-yl)phenyl]ethanone ***5b***

Melting point: 124–125 °C. ^{1}H-NMR: 1.35 (s, 3 H, CH_3), 2.35 (dt, 2 H, 6), 2.6 (s, 3 H, $CH_3C=O$), 2.65 (s, 1 H, 4), 3.5 (dd, 1 H, 4), 4.05 (dd, 1 H, 7), 5.0 (m, 1 H, 5), 7.1–7.7 (m, 8 H, ArH). ^{13}C-NMR: 20.24, 30.08, 37.16, 40.38, 52.42, 73.41, 84.32, 123.89, 125.74, 126.15, 127.47, 129.06, 129.53, 131.14, 131.19, 138.98, 143.46, 144.87, 202.45. IR: 3064, 2945, 1699, 1598, 1116, 1092. MS: 292 (M^+), 146 (base peak), 145, 91, 77, 43, 32.

6.7.1. Crystal data

$C_{20}H_{20}O_2$, M_r=292.36, colourless prismatic crystal (0.62×0.51×0.43 mm), monoclinic, space group $P2_1/c$ (No. 14) with a=10.469(2), b=8.493(2), c=17.613(4) Å, β=95.85(3)°, V=1557.9(6) Å^3, Z=4, D_c=1.247 g cm^{-3}, $F(000)$=624, μ (Mo $K\alpha$)=0.79 cm^{-1}, 2005 independent reflections measured ($2\theta \leq 45°$, T=293 K, Mo $K\alpha$ radiation, graphite monochromator, λ=0.71073 Å), on a Siemens P4 diffractometer. The structure was solved by direct methods (SHELXS 86). Refinement on F^2 (SHELXL 93) by full matrix least squares led to $wR2$=0.141, R=0.062 [for 1064 reflections with $F_0 > 4\sigma(F_0)$], S=1.016 for 247 parameters. H atoms were located in difference Fourier maps. Residual density in a final difference synthesis was within the range −0.288 to 0.357 e Å^{-3}.

6.8. (5α,6β,8α)-1-[2-(5-Ethyl-6,7,8,9-tetrahydro-5,8-epoxy-5H-benzocyclohepten-6-yl)phenyl]propanone ***5c***

Melting point: 140 °C. ^{1}H-NMR: 0.75 (t, 3 H, CH_3), 1.05 and 2.1 (m, 2 H, CH_2), 1.13 (t, 3 H, $CH_3C=O$), 2.25–2.4 (m, 2 H, CH_2), 2.55 (d, 1 H, CH_2, 4), 2.72 (m, 1 H, CH_2, 6), 2.95 (m, 1 H, CH_2, 6), 3.5 (dd, 1 H, CH_2, 4), 3.75 (dd, 1 H, CH, 7), 4.9 (m, 1 H, CH, 5), 7.05–7.45 (m, 8 H, ArH). ^{13}C-NMR: 8.91, 9.41, 25.93, 36.36, 37.70, 40.78, 53.95, 73.76, 88.29, 125.00, 126.19, 126.51, 126.85, 126.95, 129.89, 130.15, 131.04, 133.09, 140.31, 142.75, 143.26, 206.75. IR: 3074 (C–H, aromatic), 2941, 1691, 1547, 1113, 1097. MS: 320 (M^+), 173, 160, 147, 146, 132 (base peak), 91, 77, 29.

6.8.1. Crystal data

$C_{22}H_{24}O_2$, M_r=320.41, colourless prismatic crystal (0.52×0.48×0.42 mm), monoclinic, space group $P2_1/c$ (No. 14) with a=8.738(2), b=11.544(2), c=17.724(4) Å, β=97.62(3)°, V=1772.1(6) Å^3, Z=4, D_c=1.201 g cm^{-3}, $F(000)$=688, μ (Mo $K\alpha$)=0.80 cm^{-1}, 2289 independent reflections measured as for **5b** ($2\theta \leq 45°$, T=293 K). Structure solution and refinement as for **5b** led to $wR2$=0.208, R=0.082 [for 921 reflections with $F_0 > 4\sigma(F_0)$], S=1.015 for 222 parameters. H atoms were included at geometrically calculated positions. Residual density was within the range −0.171 to 0.270 e Å^{-3}.

6.9. (5a,6b,8a)-1-Phenyl-[2-(6,7,8,9-tetrahydro-5-phenyl-5,8-epoxy-5H-benzocyclohepten-6-yl)phenyl]methanone ***5d***

Melting point: 185–187 °C. ^{1}H-NMR: 2.70 (d, 1 H, 4), 3.55 (dd, 1 H, 4), 5.35 (dd, 1 H, 5), 5.50 (s, 1 H, 7), 6.04 (d, 1 H, 6), 6.65 (d, 1 H, 6), 6.90–7.30 (m, 18 H, ArH). ^{13}C-NMR: 38.00, 43.48, 55.36, 73.08, 87.73, 125.66, 126.44, 127.70, 127.95, 128.17, 128.58, 128.80, 129.21, 129.78, 129.96, 130.74, 133.13, 133.74, 137.93, 139.62, 140.52, 141.08, 142.63, 198.69. IR: 3087, 2900, 1661, 1575, 1103. MS: 416 (M^+), 398, 294, 293, 221 (base peak), 215, 208, 207, 203, 202, 195, 194, 178, 165, 115, 105, 91, 77, 49.

6.9.1. Crystal data

$C_{30}H_{24}O_2$, M_r=416.49, colourless prismatic crystal (0.57×0.47×0.44 mm), monoclinic, space group $P2_1/c$ with a=14.537(3), b=8.081(2), c=18.855(3) Å, α=90°, β=97.00(2)°, γ=90°, V=2198.5(8) Å^3, Z=4, D_c=1.282 g cm^{-3}, $F(000)$=396, μ (Mo $K\alpha$)=0.79 cm^{-1}, 3346 independent reflections measured ($2\theta \leq 45°$, T=293 K, Mo $K\alpha$ radiation, graphite monochromator, λ=0.71073 Å), on a Siemens P4 diffractometer. The structure was solved by direct methods (SHELXS 86). Refinement on F^2 (SHELXL 93) by full matrix least squares led to $wR2$=0.1633, R=0.0760 [for 1064 reflections with $F_0 > 4\sigma(F_0)$], S=1.016 for 247 parameters. H atoms were located in difference Fourier maps.

6.9.2. Crystal data for the other conformer

$C_{30}H_{24}O_2$, M_r=416.49, colourless prismatic crystal (0.57×0.47×0.44 mm), monoclinic, space group $P2_1/c$ with a=10.067(3), b=10.269(3), c=21.727(4) Å, α=90°, β=95.31(5)°, γ=90°, V=2236.5(10) Å^3, Z=4, D_c=1.237 g cm^{-3}, $F(000)$=396, μ (Mo $K\alpha$)=0.79 cm^{-1},

3648 independent reflections measured ($2\theta \leq 45°$, $T = 293$ K, Mo $K\alpha$ radiation, graphite monochromator, $\lambda = 0.71073$ Å), on a Siemens P4 diffractometer. The structure was solved by direct methods (SHELXS 86). Refinement on F^2 (SHELXL 93) by full matrix least squares led to $wR2 = 0.461$, $R = 0.0683$. H atoms were located in difference Fourier maps.

6.10. 1-Phenyl-1H-isochromene 7d

Compound **7d** was obtained as a colourless liquid. ^{1}H-NMR: 5.85 (d, 1 H, 2), 6.06 (s, 1 H, 1), 5.59 (d, 1 H, 3), 6.02–7.80 (m, 9 H, ArH). ^{13}C-NMR: 79.78, 105.49, 125.79, 126.34, 126.68, 126.95, 127.68, 128.12, 128.27, 128.43, 128.60, 130.47, 130.71, 133.97, 145,20. IR: 3072, 2900, 1599, 1261, 1065. MS: 208 (M^+), 179 (base peak), 165, 132, 103, 89, 77, 63, 51, 39.

6.11. 1-(2-Vinylphenyl)-1H-isochromene 7e

Compound **7e** was obtained as a light yellow liquid. ^{1}H-NMR: 5.27 (dd, 1 H, C=CH_2), 5.65 (dd, 1 H, C=CH_2), 5.68 (d, 1 H, 3), 6.35 (s, 1 H, 1), 6.55 (d, 1 H, aromatic), 6.60 (d, 1 H, 2), 7.04 (dd, 1 H, CH=C), 7.10–7.40 (m, 7 H, aromatic). ^{13}C-NMR: 77.56, 105.60, 116.80, 123.20, 126.50, 127.00, 128.00, 128.50, 128.85, 129.45, 130.50, 130.92, 134.65, 136.34, 137.65, 145.62. IR: 3072, 2987, 1626, 1601, 1091. MS: 234 (M^+), 233, 219 (base peak), 206, 205, 204, 203, 202, 191, 179, 178, 165, 77.

6.12. 6,7-Dihydro-5H-10b,5-oxamethanobenzo[a]-biphenylene 8e

Compound **8e** was obtained as a colourless liquid. ^{1}H-NMR: 2.06 (dd, 1 H, 4), 2.40 (dt, 1 H, 4), 2.75 (d, 1 H, 2), 3.50 (dd, 1 H, 2), 3.92 (dd, 1 H, 5), 5.12 (dd, 1 H, 3), 7.10–7.45 (m, 8 H, aromatic). ^{13}C-NMR: 35.39, 39.21, 57.75, 83.82, 90.02, 122.00, 123.35, 124.60, 125.40, 127.54, 127.95, 129.08, 130.15, 133.85, 141.20, 142.05, 149.80. IR: 3071, 1601, 1084. MS: 234 (M^+, base peak), 233, 219, 217, 216, 215, 206, 205, 204, 203, 202, 191, 189, 179, 178, 175, 128, 115, 103, 91, 89, 76, 57, 55, 51, 43, 41, 39.

6.13. Dimethyl 8,9-dihydro-5-methyl-5,8-epoxy-5H-benzocycloheptene-6,7-dicarboxylate 9b

Compound **9b** was obtained as a colourless liquid. ^{1}H-NMR: 1.80 (s, 3 H, CH_3), 2.72 (d, 1 H, 6), 3.37 (dd, 1 H, 6), 3.75 (s, 3 H, OCH_3), 5.25 (s, 3 H, OCH_3), 5.37 (d, 1 H, 5), 7.00–7.25 (m, 4 H, aromatic). ^{13}C-NMR: 18.75, 29.24, 52.40, 53.59, 78.98, 86.75, 123.11, 126.00, 128.70, 130.32, 131.87, 135.19, 139.50, 149.63, 163.08, 164.03. IR: 2954, 1718, 1435, 1142. MS: 289 ($M^+ + 1$), 149, 146, 145 (base peak), 132, 43.

6.14. Dimethyl 5-(2-vinylphenyl)-8,9-dihydro-5,8-epoxy-5H-benzocycloheptene-6,7-dicarboxylate) 9e

Compound **9e** was obtained as a yellow oil. ^{1}H-NMR: 2.75 (d, 1 H, 5), 3.52 (dd, 1 H, 5), 3.76 (s, 3 H, OCH_3), 3.79 (s, 3 H, OCH_3), 4.85 (dd, 1 H, vinylic CH_2), 5.43 (dd, 1 H, 4), 5.53 (d, 1 H, vinylic CH_2), 6.66 (dd, 1 H, vinylic CH), 6.76–7.62 (m, 8 H, aromatic). ^{13}C-NMR: 29.02, 52.64, 52.67, 79.44, 93.51, 114.56, 125.5., 127.07, 127.77, 127.88, 128.63, 129.50, 130.24, 130.76, 134.16, 135.80, 136.00, 138.53, 139.60, 149.18, 162.85, 165.13. IR: 3070, 3028, 2955, 1729, 1638, 1086. MS: 376 (M^+), 131 (base peak), 118, 103.

6.15. Dimethyl 5-acetyl-3,4-dihydro-4-[3-methoxy-1-(methoxycarbonyl)-3-oxopropenyl]naphthalene-1,2-dicarboxylate 10b

Compound **10b** was obtained as colourless crystals melting at 132 °C. ^{1}H-NMR: 2.54 (s, 3 H, CH_3CO), 2.61 (dd, 1 H, 2), 3.15 (d, 1 H, 2), 3.58 (s, 3 H, CO_2CH_3), 3.78 (s, 3 H, CO_2CH_3), 3.80 (s, 3 H, CO_2CH_3), 3.91 (s, 3 H, CO_2CH_3), 4.80 (d, 1 H, 1), 5.22 (s, 1 H, vinylic CH), 7.72–7.78 (m, 4 H, aromatic). ^{13}C-NMR: 26.37, 29.85, 36.09, 51.96, 52.66, 52.84, 121.30, 125.91, 128.35, 129.93, 131.25, 131.91, 134.06, 137.60, 139.59, 149.75, 165.34, 165.75, 168.34, 168.37, 200.68. IR: 3003, 2954, 1737, 1693, 1435, 1114. MS: 430 (M^+), 398, 355, 354, 353 (base peak), 339, 325, 323, 311, 255, 59, 43.

6.15.1. Crystal data

$C_{22}H_{22}O_9$, $M_r = 430.40$, colourless prismatic crystals ($0.64 \times 0.31 \times 0.34$ mm), triclinic, space group P1 with $a = 8.697(4)$, $b = 11.228(4)$, $c = 11.345(5)$ Å, $\alpha = 82.02(3)°$, $\beta = 82.62(4)°$, $\gamma = 79.33(3)°$, $V = 1072.1(8)$ Å^3, $Z = 2$, $D_c = 1.333$ g cm^{-3}, $F(000) = 452$, μ (Mo $K\alpha$) = 0.79 cm^{-1}, 3783 independent reflections measured ($2\theta \leq 45°$, $T = 293$ K, Mo $K\alpha$ radiation, graphite monochromator, $\lambda = 0.71073$ Å), on a Siemens P4 diffractometer. The structure was solved by direct methods (SHELXS 86). Refinement on F^2 (SHELXL 93) by full matrix least squares led to $wR2 = 0.0700$, $R = 0.046$. H atoms were located in difference Fourier maps.

6.16. 5-(2-Vinylbenzoyl)-3,4-dihydro-1,1,2,2-naphthalenetetracarbonitrile 11e

Compound **11e** was obtained as brown crystals melting between 102 °C and 106 °C. ^{1}H-NMR: 3.21 (t, 2 H, 1), 3.58 (t, 2 H, 2), 5.30 (dd, 1 H, vinylic CH_2), 5.80 (dd, 1 H, vinylic CH_2), 7.10 (dd, 1 H, vinylic CH), 7.45–8.25 (m, 7 H, aromatic). ^{13}C-NMR: 28.37, 28.95, 75.33, 80.50, 96.82, 121.47, 126.33, 126.58, 127.87, 127.66, 128.53, 129.01, 129.22, 129.33, 129.41, 129.60, 129.93, 130.24, 130.66, 133.17, 133.93, 142.17, 198.25. IR: 3090, 2928, 2248, 1664,

1596. MS: 363 (M^+), 362 (base peak), 361, 318, 131, 103, 77, 51, 43.

6.16.1. Crystal data

$C_{23}H_{14}N_4O$, $M_r = 362.38$, yellow rhombic crystals (0.63×0.16×0.15 mm), orthorhombic, space group $Pna2_1$ with $a = 21.490(4)$, $b = 10.886(4)$, $c = 8.086(1)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 1888.2(7)$ Å^3, $Z = 4$, $D_c = 1.275$ g cm^{-3}, $F(000) = 752$, μ (Mo $K\alpha$) = 0.79 cm^{-1}, 1323 independent reflections measured ($2\theta \leq 45°$, $T = 293$ K, Mo $K\alpha$ radiation, graphite monochromator, $\lambda = 0.71073$ Å) on a Siemens P4 diffractometer. The structure was solved by direct methods (SHELXS 86). Refinement on F^2 (SHELXL 93) by full matrix least squares led to $wR2 = 0.0651$, $R = 0.0413$. H atoms were located in difference Fourier maps.

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