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β–α Photoisomerization of Cobaloxime Complexes in the Solid State. I. Different Reaction Rates in Polymorphic Crystals

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Abstract

Two crystalline forms of (β-cyanoethyl)bis(dimethylglyoximato)(3-methylpyridine)cobalt(III) (dimethylglyoximato = 2,3-butanedione dioximato), $C_{17}H_{25}CoN_6O_4$, $[Co(C_3H_4N)(C_4H_7N_2O_2)_2(C_6H_7N)]$, were obtained from methanol solutions. Form I: $M_r = 436.36$, monoclinic, $P2_1/a$, $a = 23.742$ (5), $b = 9.496$ (2), $c = 8.819$ (1) Å, $\beta = 94.59$ (2)°, $V = 1981.9$ (6) Å^3, $Z = 4$, $D_x = 1.463$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 8.42$ cm^{-1}, $F(000) = 912$, $T = 298$ K, $R = 0.057$ for 3955 observed reflections; form II: monoclinic, $P2_1/a$, $a = 21.425$ (4), $b = 9.290$ (1), $c = 11.517$ (2) Å, $\beta = 117.58$ (2)°, $V = 2031.6$ (7) Å^3, $Z = 4$, $D_x = 1.427$ g cm^{-3}, λ (Mo $K\alpha$) = 0.71069 Å, $\mu = 8.22$ cm^{-1}, $F(000) = 912$, $T = 298$ K, $R = 0.048$ for 4198 observed reflections. The rate of β–α isomerization for form II was much greater than that for form I. The structure analysis has shown that the conformations of the β-cyanoethyl groups in forms I and II are almost the same and that there is greater room around the cyanoethyl group in form II than in form I.

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Introduction

The β-cyanoethyl group, $-CH_2CH_2CN$ (1), in the complexes of bis(dimethylglyoximato)cobalt(III), cobaloximes, isomerizes to the α-cyanoethyl group, $-C^*H(CH_3)CN$ (2), on irradiation of powdered samples with visible light (Ohgo & Takeuchi, 1985).
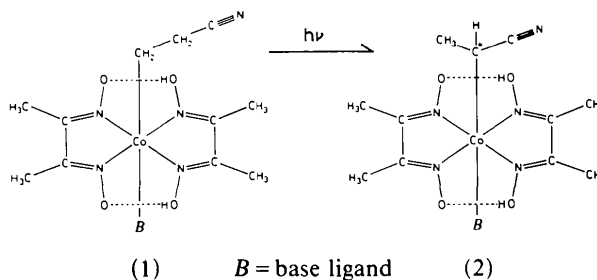
(1)   *B* = base ligand   (2)

The photoreaction occurs only in the solid state and the reverse reaction is not observed. This finding has stimulated us to make serial studies of (β-cyanoethyl)cobaloxime with different base ligands, because the relation between crystal structure and reactivity in the solid state has been our main interest since the crystalline-state racemization of (α-

cyanoethyl)cobaloximes was first observed (Ohashi & Sasada, 1977). Powdered specimens of (β-cyanoethyl)(triphenylphosphine)cobaloxime taken from different crystallization batches revealed various isomerization rates (Kato, 1984). Closer examination showed that they were a mixture of four crystalline forms of the complex present in a ratio dependent on crystallization conditions. The different isomerization rates of the four forms could be explained qualitatively in terms of the respective crystal structures. However, quantitative determination of the reaction rate of each form has not yet been achieved because attempts to obtain four forms separately were unsuccessful. Recently we have found that (β-cyanoethyl)(3-methylpyridine)cobaloxime has two crystalline forms, and have obtained them separately. The present paper reports the isomerization and crystal structures of the two crystalline forms.

Experimental

The title complex was synthesized by the method reported previously by Ohgo, Takeuchi, Natori, Yoshimura, Ohashi & Sasada (1981). Hot methanol solutions were allowed to stand at room temperature and crystals of forms I or II, or even a mixture of the two forms were obtained by accident. Detailed crystallization conditions for each form have not yet been specified.

Form I

Orange thin plate-like crystals. Preliminary unit-cell dimensions and the space group determined from photographs; systematic absences $h = 2n + 1$ for $h0l$ and $k = 2n + 1$ for $0k0$. Crystal size $0{\cdot}1 \times 0{\cdot}4 \times 0{\cdot}6$ mm, Rigaku four-circle diffractometer; Mo $K\alpha$ monochromated by graphite, unit-cell dimensions from 2θ values of 18 reflections in the range $20 < 2\theta < 30°$. Intensities measured up to $2\theta = 55°$; range of hkl -30 to 30, 0 to 12 and 0 to 11, $\omega/2\theta$ scan mode, scan rate $4°(\theta)$ min^{-1}, scan width $(1{\cdot}0 + 0{\cdot}35 \tan \theta)°$, stationary background counts accumulated for 5 s before and after each scan, three standard reflections $\bar{9}40$, 051 and $10{,}0{,}2$, intensity variation $0{\cdot}997$ to $1{\cdot}016$. 4553 independent reflections, of which 3955 with $|F_o| > 3\sigma(|F_o|)$ used for structure determination. No absorption correction.

Structure solved by direct methods using MULTAN78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), refined by full-matrix least squares with SHELX76 (Sheldrick, 1976). Positions of all H atoms obtained from a difference map. Anisotropic and isotropic thermal parameters for the non-H atoms and for H atoms, respectively. $\sum w(|F_o| - |F_c|)^2$ minimized with $w = [\sigma(|F_o|)^2 + 0{\cdot}002210(|F_o|)^2]^{-1}$;$(\Delta/\sigma)_{max} = 0{\cdot}3$;$\Delta\rho_{max} = 0{\cdot}6$ e Å^{-3}; $R = 0{\cdot}057$ and $wR = 0{\cdot}079$, $S = 0{\cdot}950$. The

Table 1. *Final atomic coordinates* ($\times 10^5$ *for* Co; $\times 10^4$ *for* C, N *and* O) *and equivalent isotropic thermal parameters* (Å^2) *for form* I

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

	x	y	z	B_{eq}
Co	63989 (2)	16703 (4)	79723 (5)	2·2
N(1)	6112 (1)	1565 (3)	9887 (3)	2·9
N(2)	6193 (1)	−257 (3)	7927 (3)	2·6
N(3)	6698 (1)	1787 (3)	6062 (3)	2·6
N(4)	6612 (1)	3583 (3)	8019 (3)	2·7
O(1)	6105 (1)	2679 (3)	10844 (3)	4·0
O(2)	6295 (1)	−1101 (2)	6786 (3)	3·3
O(3)	6721 (1)	670 (3)	5099 (3)	3·3
O(4)	6554 (1)	4415 (3)	9242 (3)	3·7
C(1)	5915 (2)	364 (4)	10285 (4)	3·0
C(2)	5963 (1)	−722 (3)	9131 (4)	2·9
C(3)	6845 (1)	3023 (4)	5612 (4)	2·7
C(4)	6800 (1)	4090 (3)	6801 (4)	2·7
C(5)	5678 (2)	97 (5)	11782 (5)	4·4
C(6)	5780 (2)	−2216 (4)	9308 (5)	4·0
C(7)	7049 (2)	3337 (4)	4094 (5)	3·9
C(8)	6991 (2)	5580 (4)	6632 (5)	4·2
N(5)	5619 (1)	2254 (3)	6967 (3)	2·4
C(9)	5314 (1)	3296 (3)	7519 (4)	3·0
C(10)	4799 (1)	3757 (4)	6848 (4)	3·4
C(11)	4591 (2)	3075 (4)	5539 (5)	4·0
C(12)	4896 (2)	2015 (5)	4953 (4)	3·8
C(13)	5408 (1)	1624 (4)	5685 (4)	3·0
C(17)	4483 (2)	4933 (5)	7543 (6)	5·3
C(14)	7152 (1)	998 (4)	8918 (4)	3·1
C(15)	7630 (2)	2043 (4)	9279 (5)	3·8
C(16)	7938 (2)	2412 (5)	7957 (5)	4·3
N(6)	8197 (2)	2672 (6)	6972 (6)	6·9

atomic parameters for the non-H atoms are given in Table 1.

Form II

Orange plate-like crystals. Experimental details are almost the same as those for form I. Crystal size $0{\cdot}2 \times 0{\cdot}3 \times 0{\cdot}4$ mm. Unit-cell dimensions from 2θ values of 18 reflections in the range $27 < 2\theta < 30°$. Intensities measured up to $2\theta = 55°$, range of hkl -27 to 24, 0 and 12 and 0 to 14, three standard reflections $12{,}0{,}1$, $\bar{9}51$ and $\bar{2}37$, intensity variation $0{\cdot}987$ to $1{\cdot}005$, 4604 reflections, of which 4198 with $|F_o| > 3\sigma(|F_o|)$ used for structure determination.

Structure solved by direct methods, refined by full-matrix least squares. The difference map showed a disorder of the β-cyanoethyl group. Positions for all H atoms except those of the minor cyanoethyl group obtained from the subsequent difference map. The occupancy factors of disordered cyanoethyl groups also refined. The cyanoethyl groups were loosely constrained to have the structure observed in the related complexes. Anisotropic and isotropic thermal parameters for non-H atoms except those of the minor cyanoethyl group and H atoms, respectively. $\sum w(|F_o| - |F_c|)^2$ minimized with $w = [\sigma(|F_o|)^2 + 0{\cdot}001047(|F_o|)^2]^{-1}$; $(\Delta/\sigma)_{max} = 0{\cdot}5$; $\Delta\rho_{max} = 0{\cdot}6$ e Å^{-3}; $R = 0{\cdot}048$ and $wR = 0{\cdot}075$ for 4198

Table 2. *Final atomic coordinates* ($\times 10^5$ *for* Co; $\times 10^4$ *for* C, N *and* O; $\times 10^3$ *for primed atoms*) *and equivalent isotropic thermal parameters* (Å^2) *for form* II

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

	x	y	z	B_{eq}
Co	59198 (2)	28056 (4)	34908 (3)	2·5
N(1)	6108 (1)	2690 (3)	2049 (3)	3·5
N(2)	5782 (1)	4750 (3)	2988 (2)	3·0
N(3)	5775 (1)	2934 (3)	4970 (2)	3·0
N(4)	6072 (1)	864 (3)	4015 (3)	3·1
O(1)	6309 (2)	1445 (3)	1701 (3)	5·2
O(2)	5606 (1)	5751 (2)	3625 (2)	4·3
O(3)	5642 (1)	4183 (3)	5404 (2)	4·3
O(4)	6258 (1)	−143 (2)	3381 (3)	4·6
C(1)	6057 (2)	3861 (4)	1417 (3)	3·7
C(2)	5851 (2)	5098 (3)	1962 (3)	3·4
C(3)	5812 (1)	1744 (4)	5598 (3)	3·2
C(4)	5990 (2)	507 (3)	5016 (3)	3·4
C(5)	6218 (3)	3968 (6)	283 (4)	5·7
C(6)	5736 (2)	6582 (4)	1399 (4)	4·9
C(7)	5722 (2)	1678 (6)	6808 (4)	5·3
C(8)	6105 (2)	−979 (4)	5570 (4)	5·1
N(5)	4858 (1)	2400 (3)	2309 (2)	3·1
C(9)	4360 (2)	3212 (4)	2368 (3)	3·5
C(10)	3638 (2)	2975 (4)	1611 (3)	4·4
C(11)	3446 (2)	1845 (5)	753 (4)	5·2
C(12)	3950 (2)	990 (4)	667 (3)	5·0
C(13)	4641 (2)	1297 (4)	1454 (3)	4·0
C(17)	3114 (2)	3948 (6)	1752 (5)	6·4
C(14)	6939 (1)	3345 (4)	4612 (3)	4·2
C(15)	7479 (2)	2260 (4)	5461 (4)	4·2
C(16)	7461 (2)	1896 (6)	6690 (4)	6·3
N(6)	7469 (2)	1643 (7)	7659 (4)	8·0
C(15′)	732 (1)	342 (2)	605 (1)	6·5 (5)
C(16′)	737 (1)	196 (2)	666 (2)	5·9 (4)
N(6′)	745 (1)	118 (1)	747 (1)	5·4 (4)

reflections, $S = 0.724$. The atomic parameters for non-H atoms are given in Table 2.*

Atomic scattering factors including the anomalous-dispersion terms were taken from *International Tables for X-ray Crystallography* (1974). Calculations were carried out on a FACOM-HITAC system M-270H computer at this Institute.

β-α isomerization

KBr pellets which contained 1% of the *β*-complex were exposed to visible light with a 500 W Hg lamp under an argon atmosphere: the absorption at $2237\ \text{cm}^{-1}$, which was assigned to ν_{CN} of the *β*-cyanoethyl group, decreased, and the absorption of ν_{CN} of the *α*-cyanoethyl group at $2204\ \text{cm}^{-1}$ increased with irradiation time. Conversion curves were obtained from the change of the absorption at $2237\ \text{cm}^{-1}$.

* Lists of anisotropic thermal parameters for non-H atoms, positional and thermal parameters for H atoms, bond distances and angles and structure factors for forms I and II have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44236 (43 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Results and discussion

Crystal structure

The crystal structures of forms I and II are shown in Fig. 1. Forms I and II have the same space group, $P2_1/a$, and the molecular arrangements in both crystals are similar to each other. The reactive cyanoethyl groups in both crystals are in contact with those of neighbouring molecules related by a screw operation. There are no unusually short contacts in both crystal structures except for the minor cyanoethyl group [C(15′)–O(4), 3·10 (2) Å].

Molecular structure

The molecular structures in forms I and II with the numbering of the atoms are shown in Fig. 2. Selected bond distances and angles and torsion angles around the Co–C, Co–N and C(14)–C(15) bonds are listed in Table 3. In form II, the cyanoethyl group is disordered. The occupancy factors of the two conformers are 0·817 (6) and 0·183 (6), respectively. The atoms of the minor cyanoethyl group are hatched. The two conformers are approximately related by a mirror plane through a long axis of the cobaloxime skeleton. The cyanoethyl groups in forms I and II, except the minor group in the latter, have almost the same conformation, while the orientations of the 3-methyl-pyridine ligands are significantly different in the two forms.

β-α isomerization

Fig. 3 shows the conversion curves for *β-α* isomerization of forms I and II. The reaction rate of form II is remarkably greater than that of form I. Since the conformations of the cyanoethyl groups in both crystals are nearly the same, the difference in the reaction rates must be caused by the environment
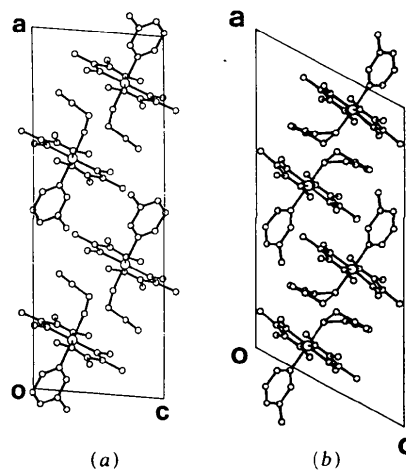

Fig. 1. Crystal structures of (*a*) form I and (*b*) form II, viewed along the *b* axis.

of the cyanoethyl groups. To make an estimation of the effects of the environment, we have drawn a 'cavity' for the β-cyanoethyl groups in the two crystal forms, which is defined as free space for reactive groups in crystals and was very useful in the studies of the crystalline-state racemization of cobaloximes (Ohashi, Uchida, Sasada & Ohgo, 1983).

Fig. 4 shows the cavities for the cyanoethyl groups in forms I and II. The upper figures are views along the normal to the cobaloxime plane and the lower ones are side views, where the molecular skeletons are incorporated. The shapes of the cavities are significantly different from each other; this is caused by the presence of the disordered structure. The volumes of the cavities for forms I and II were calculated to be 10·36 and 11·88 Å^3, respectively. An increase of the space for movement of β-cyanoethyl group and for accommodation of the α-cyanoethyl group produced should facilitate the progress of the isomerization. Thus, the interpretation in terms of 'cavities' can also be successfully applied to the present isomerization in the solid state. In normal solid-state reactions, crystals collapse with progress of reactions because the reactions occur at crystal surfaces. On the other hand, the results described above suggest that the isomerization proceeds to some extent without degradation of crystallinity.
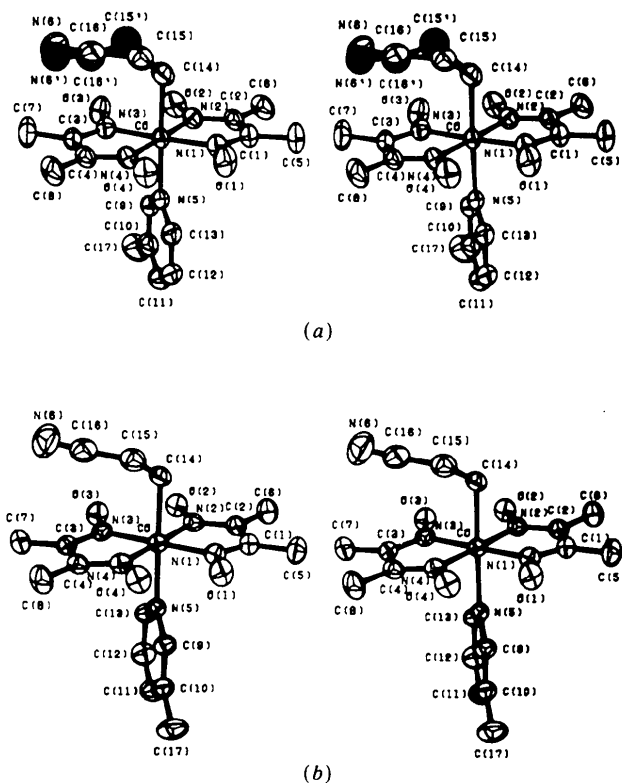
Table 3. *Selected bond distances* (Å), *angles* (°) *and torsional angles* (°) *for forms* I *and* II

	Form I	Form II
Co–N(1)	1·875 (3)	1·884 (3)
Co–N(2)	1·894 (3)	1·878 (3)
Co–N(3)	1·883 (3)	1·871 (3)
Co–N(4)	1·886 (3)	1·882 (3)
Co–N(5)	2·065 (3)	2·075 (3)
Co–C(14)	2·016 (4)	2·019 (3)
N(1)–Co–N(2)	81·7 (1)	81·4 (1)
N(3)–Co–N(4)	81·0 (1)	81·1 (1)
N(1)–Co–N(4)	98·6 (1)	98·8 (1)
N(2)–Co–N(3)	98·8 (1)	98·7 (1)
N(1)–Co–C(14)	89·2 (1)	88·2 (1)
N(1)–Co–N(5)	91·2 (1)	91·6 (1)
N(2)–Co–C(14)–C(15)	176·7 (3)	179·3 (3)
N(2)–Co–C(14)–C(15')		110·1 (11)
N(2)–Co–N(5)–C(9)	131·5 (3)	−50·1 (3)
Co–C(14)–C(15)–C(16)	−81·1 (4)	−77·4 (5)
Co–C(14)–C(15')–C(16')		64·1 (17)

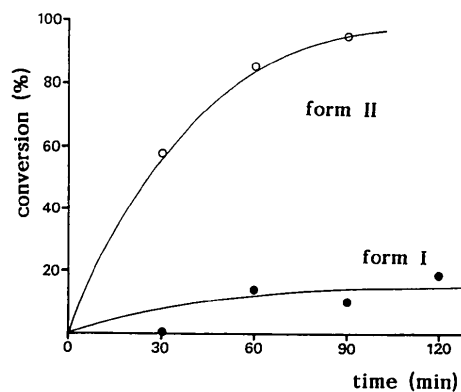Fig. 3. β-α isomerization of the cyanoethyl group. Approximate first-order reaction curves are obtained by least-squares fitting using the observed values. The rate constants are 0.3×10^{-4} s^{-1} for form I and 5.3×10^{-4} s^{-1} for form II.

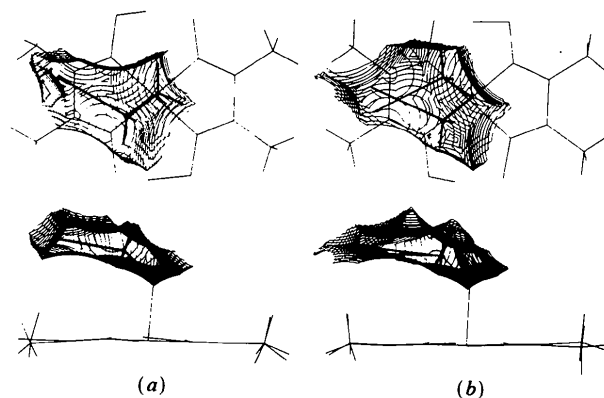Fig. 2. Stereoscopic drawings (ORTEP, Johnson, 1965) of (a) form I and (b) form II.

Fig. 4. Cavities for the cyanoethyl group viewed along the normal to the mean plane of cobaloxime and parallel to the plane in (a) form I and (b) form II. Contours are drawn in sections separated by 0·1 Å.

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Reaction Pathway in the Photoconversion of a Tetrahydroanthracenedione (I) to its Solid-State Photoproduct (II)

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Abstract

$C_{18}H_{20}O_2$, $M_r = 268 \cdot 36$, $F(000) = 576$, $T = 295$ K, Mo $K\alpha_1$, $\lambda = 0 \cdot 70930$ Å. (I) 2,3,4aβ,10aβ-Tetra-methyl-4a,5,10,10a-tetrahydrobenzo[6,7]naphtho-1,4-quinone (2,3,4a,9a-tetramethyl-cis-4a,9,9a,10-tetrahydro-1,4-anthracenedione), monoclinic, Cc, $a = 6 \cdot 877$ (2), $b = 22 \cdot 377$ (3), $c = 9 \cdot 972$ (3) Å, $\beta = 101 \cdot 68$ (1)°, $V = 1502 \cdot 8$ (6) Å^3, $Z = 4$, $D_x = 1 \cdot 186$ g cm^{-3}, $\mu = 0 \cdot 71$ cm^{-1}, $R = 0 \cdot 037$ for 821 observed reflections. The conformation of molecule (I) is twisted such that the bridgehead methyl groups are staggered with a torsion angle of 61·0°. Bond lengths and angles are close to normal values. (II) 1,3,4,6-Tetramethylbenzo[8,9]tricyclo[4.4.0.0^{3,10}]-dec-8-ene-2,5-dione, triclinic, $P\bar{1}$, $a = 9 \cdot 825$ (2), $b = 12 \cdot 369$ (3), $c = 12 \cdot 894$ (3) Å, $\alpha = 107 \cdot 39$ (1), $\beta = 92 \cdot 85$ (2), $\gamma = 96 \cdot 79$ (1)°, $V = 1478 \cdot 8$ (6) Å^3, $Z = 4$ (two molecules per asymmetric unit), $D_x = 1 \cdot 205$ g cm^{-3}, $\mu = 0 \cdot 72$ cm^{-1}, final $R = 0 \cdot 055$ for 3850 observed reflections. Bond lengths and angles suggest a strained system. Compound (II) is the only solid-state photoproduct of (I). The crystal structures of diketones (I) and (II) allow the proposal of a detailed reaction pathway for the formation of (II). The proposed mechanism involves a γ-H-atom abstraction by an ethylenic C atom to form an intermediate biradical, followed by C-C bonding to generate the tricyclic compound (II). The complete reaction pathway involves a minimum of intramolecular motion, with an accompanying movement of the whole reacting molecule by about 1·0 Å allowing accommoda-
tion of the photoproduct in the reactant lattice, in a topochemically favourable process.

Introduction

Photolysis of crystals of (I) gives only product (II), while photolysis in solution gives mainly (II) at high temperature and predominantly (III) at low temperature. The crystal structure of (I) has been determined in an effort to rationalize the observed photochemical behaviour, and that of (II) to provide details of possible reaction pathways.
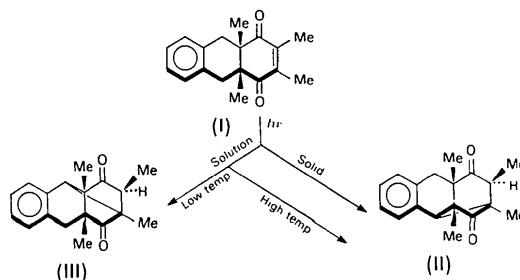
Experimental

Crystal size $0 \cdot 4 \times 0 \cdot 4 \times 0 \cdot 2$ mm for (I) [$0 \cdot 4 \times 0 \cdot 4 \times 0 \cdot 5$ mm for (II)], m.p. 357-358 K [362-363 K], Enraf-Nonius CAD-4 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, lattice parameters from setting of 25 reflections with $10 \leq \theta \leq 18°$ [$20 \leq \theta \leq 23°$]. 1312 unique reflections with $\theta \leq 25°$ for (I)