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The Crystal and Molecular Structure of $\Delta^{1,1'}$-Dicyclohexenyl Ketone

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Crystals of $\Delta^{1,1'}$-dicyclohexenyl ketone, $C_{13}H_{18}O$, are triclinic, space group $P\bar{1}$. The 2152 data were taken at −110°C. Cell dimensions are $a=9{\cdot}388$ (3), $b=8{\cdot}693$ (5), $c=9{\cdot}385$ (3) Å, $\alpha=104{\cdot}85$ (3), $\beta=113{\cdot}77$ (3), $\gamma=117{\cdot}16$ (2)°. The structure was determined by direct methods and has been refined to an R value of 5·1 %. The structure is partially disordered at room temperature. The crystals are colorless, but show a reversible photochromic change when subjected to near-ultraviolet radiation. Although the crystals undergo the same color change at low temperature, the reaction is not reversible and the crystals remain colored indefinitely at −110°C. Therefore, in addition to the data collected on the crystal in its colorless form, a data set was collected on the compound in its pink form at low temperature in an attempt to see a change in conformation or structure. A half-normal probability plot indicates no difference between the positional parameters derived from the two data sets. Both a short intramolecular and a short intermolecular distance are observed between the carbonyl oxygen atom and a hydrogen atom.

Introduction

Crystals of $\Delta^{1,1'}$-dicyclohexenyl ketone (DCK) undergo a reversible photochromic change when subjected to near-ultraviolet radiation. The crystals change from colorless to pink to a deep red depending on the length and intensity of irradiation. The process is readily reversible at room temperature, the crystals losing their color in a matter of minutes when removed from the exciting light. The formation of colored product with irradiation proceeds readily at low temperature, indicating a photochemical reaction. However, the loss of color is apparently a thermal process since the crystals when maintained at a low temperature (less than 0°C) after being irradiated, were seen to remain in the colored form indefinitely.

Several studies of photochromic reactions have been reported in the literature. Photochromism through partial torsion about an essential double bond in bianthrones was studied by Korenstein, Muskzat & Sharafy-Ozeri (1973). An irreversible photochromic reaction of *p*-nitrophenol was studied by X-ray crystallography by Coppens (1960). An intermolecular reaction was determined to be the basis of the photochromic change in this case. The crystal structures of of 2-(2′,4′-dinitrobenzyl)pyridine and 4-(2′,4′-dinitrobenzyl)pyridine have been determined (Seff & Trueblood, 1968; Otterson & Seff, 1974) to elucidate the reversible photochromic change observed in the former. An intramolecular tautomeric reaction in which a methylene hydrogen is transferred to the oxygen of the *o*-nitro group and then to the pyridine nitrogen is postulated on the basis of these structural determinations.

Lehr (1968) studied cyclization reactions of $\Delta^{1,1'}$ dicyclohexenyl ketone, a cross-conjugated dienone, in order to resolve the question of conrotatory *versus* disrotatory ring closure across C(2)–C(2′). Conrotatory closure was observed for the acid-catalyzed reaction, whereas disrotatory closure was observed for the photochemical reaction in solution. The reaction products for the photolysis in benzene indicated that hydrogen abstraction at C(6) [C(6′)], by the carbonyl O(8) may be involved in the cyclization reaction.

We have determined the structure of the colorless-form of $\Delta^{1,1'}$-dicyclohexenyl ketone at room temper-

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ature and at −110°C and in the pink form at −110°C to see if a difference could be observed in the structures. If no difference could be observed it was hoped that an accurate determination of the crystal structure would indicate whether the photochromic change is caused by an inter- or intramolecular reaction and perhaps would suggest a mechanism.

Experimental

Crystals of $\Delta^{1,1'}$-dicyclohexenyl ketone were grown originally by dissolving a sample of DCK in methanol, adding water until the solution became cloudy and allowing it to stand. Crystals grown in this manner appeared excellent, but a high percentage were found to be twinned. A crystal was selected which was not twinned and the space group determined to be $P\bar{1}$ on a G.E. XRD-5 diffractometer. It was necessary to put the crystal in a capillary in order to take data as the crystals gradually sublimed at room temperature, losing all diffracted intensities in 1–2 days. Data were collected and the structure was solved at room temperature in this manner, but as discussed in the next section refinement was not satisfactory because of disorder. It was suspected that this was a type of disorder associated with high thermal motion and we therefore decided to recollect the data at low temperature (−110°C). Since the basic manner of data collection and processing was the same at both room and low temperatures a full description is only given for the low temperature data.

Table 1. *Crystallographic data*

Formula $C_{13}H_{18}O$	Space group $P\bar{1}$
F.W. 190·28	$Z=2$
$F(000)=208$	
$D_{\text{exp}}=1{\cdot}120$ g cm^{-3} (room temperature)*	
$D_{\text{calc}}=1{\cdot}138$ g cm^{-3} (room temperature), H_2O and NaCl solution flotation.	
a_{lt}† $=9{\cdot}388$ (3) Å	a_{rt}‡ $=9{\cdot}4909$ (6) Å
$b_{\text{lt}}=8{\cdot}693$ (4)	$b_{\text{rt}}=8{\cdot}8044$ (4)
$c_{\text{lt}}=9{\cdot}385$ (3)	$c_{\text{rt}}=9{\cdot}4801$ (4)
$\alpha_{\text{lt}}=104{\cdot}85$ (3)°	$\alpha_{\text{rt}}=103{\cdot}502$ (4)°
$\beta_{\text{lt}}=113{\cdot}77$ (3)	$\beta_{\text{rt}}=113{\cdot}103$ (4)
$\gamma_{\text{lt}}=117{\cdot}16$ (2)	$\gamma_{\text{rt}}=117{\cdot}658$ (4)
$V_{\text{lt}}=524{\cdot}62$ Å^3	$V_{\text{rt}}=555{\cdot}08$ Å^3

* Discrepancy between D_{exp} and D_{calc} is probably caused by incomplete wetting of the crystals.

† lt: low temperature.

‡ rt: room temperature (27°C).

Large crystals of DCK had been grown by sublimation. In an attempt to overcome the problem of twinning, crystals of sublimed DCK were cut to appropriate dimensions and mounted on a glass fiber. Since at low temperature loss of intensity due to sublimation was not a problem no capillary was used. No twinning was seen in these crystals. Data were then re-collected on a Nonius CAD-4 automatic diffractometer equipped with a low-temperature unit. The least-squares cell dimensions were determined from averages of the $+2\theta$ and -2θ values of 40 reflections, distributed throughout reciprocal space, measured at −110°C. The crystallographic data are shown in Table 1. The 2152 data, including all unique reflections with θ less than 75°, were taken with Ni-filtered Cu $K\alpha$ radiation ($\lambda=1{\cdot}54178$ Å). The data were collected with θ–2θ scans in which the θ scan width was between 1·00 and 1·38°. The 011 and $1\bar{2}0$ reflections were excluded from the data, because of the large intensities and high extinction effects. The maximum scan time was 90 s, with $\frac{2}{3}$ of the time spent scanning the peak and $\frac{1}{6}$ each on the left and right backgrounds. There were 19 reflections which had intensities we considered indistinguishable from the background on the basis that the net count was less than $1{\cdot}4T^{1/2}$ (T = total count). These reflections were assigned intensities equal to $0{\cdot}7T^{1/2}$ for purposes of least-squares refinement. Lorentz and polarization corrections were applied to the data. No absorption corrections were made. Each amplitude was assigned a weight given by $w_f=1/\sigma_F^2$, where the standard deviation σ_F of the amplitude was calculated by

$$\sigma_F=\tfrac{1}{2}\left[\frac{\sigma^2+[(0{\cdot}02)P]^2}{(\mathrm{Lp})P}\right]^{1/2},$$

in which $\sigma=T^{1/2}V$, V = scan speed, $P=[PK-2(R+L)]V$, PK = peak count, R = right background count, L = left background count, Lp = Lorentz–polarization factor.

Secondary extinction corrections were made on the observed intensities according to the equation $I_{\text{corrected}}=I_o\exp(-c_{\text{ext}}P)$. The constant c_{ext} was determined to be 0·000005 from the slope of a plot of $\log F_c/F_o$ *versus* P (net count) for 38 reflections with F_o greater than 10.

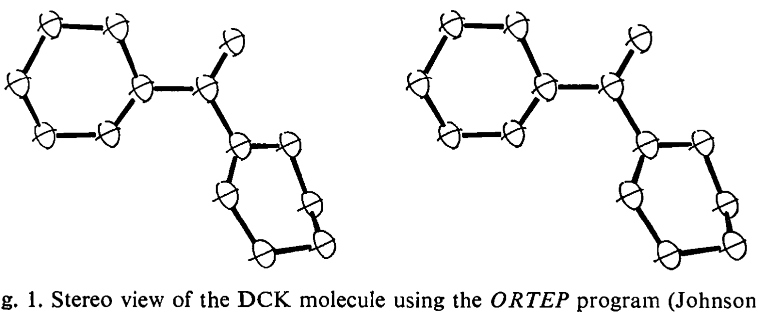

Fig. 1. Stereo view of the DCK molecule using the *ORTEP* program (Johnson, 1965).

Next an attempt was made to collect a data set on a crystal in its pink form. A mounted crystal was exposed to bright sunlight on a cool day for a period of about 15 min, after which the crystal had a deep pink color. The crystal was quickly placed in the cold stream of the diffractometer system where it retained its color. Another data set was collected in this manner; however, several crystals were used since the irradiation apparently weakened the structure, causing the crystals to fracture and break apart under the force of the cold stream, an effect not observed with crystals in the clear form. Data were collected and reduced in the same manner as described for the colorless form data. Least-squares cell dimensions were not significantly different from those of the colorless form. A total of 79 reflections were not distinguishable from the background and were treated as described above. The weighting scheme was identical to that used previously. Extinction was not apparent and these corrections were therefore not made for this data set.

Structure solution and refinement

The structure was solved by the symbolic addition procedure (Karle & Karle, 1966) using the normalized structure factors derived from the amplitudes of the data set collected at room temperature. The distribution and statistics of the $|E|$'s agree with the theoretical values for the centrosymmetric case. The 164 highest $|E|$'s (greater than 1·65) were used to generate triplets satisfying the $\sum_2$ relation. The origin was defined by assigning a positive sign to the $52\bar{6}$ and $\bar{2}41$ reflections and a negative sign to the $1\bar{5}7$ reflection. The symbol A was assigned to the $\bar{6}06$ reflection, B to $7\bar{3}1$ and C to $61\bar{5}$. The signs of B and C were determined to be negative; the sign of A was undetermined. Signs of 164 E's were generated using a minus sign for A, B and C. The E map calculated from these signed E values yielded a reasonable structure. The carbon and oxygen atom positions from the E map were used with isotropic thermal parameters in a structure-factor calculation and refined by block-diagonal least-squares minimization of $\sum w_f(|F_o|-|F_c|)^2$. The hydrogen atoms were located from geometrical considerations with the aid of a difference Fourier synthesis. The hydrogen atoms were included in the structure-factor least-squares refinement with isotropic temperature factors. The temperature factors for the non-hydrogen atoms were made anisotropic. The refinement appeared to converge at an $R=(\sum||F_o|-|F_c||/\sum|F_o|)$ of 0·14. At this point the calculated bond distances between C(4′) and C(5′) and between C(4) and C(5) were 1·446 and 1·499 Å respectively. The major axes of the thermal ellipsoids had values as high as 16·8 and 13·0 Å^2 for atoms C(5′) and C(4′) and 9·3 and 10·2 Å^2 for C(4) and C(5). These observations indicated that disorder or a high thermal vibration existed at C(4′) and C(5′) and to a lesser extent at C(4) and C(5). It was not apparent from a difference map whether the atoms were truly disordered or had a large thermal vibration. Attempts to resolve

Table 2. *Atomic fractional coordinates and thermal parameters* (*all* $\times 10^4$)

The temperature factor is expressed in the form $\exp\{-(h^2b_{11}+k^2b_{22}+l^2b_{33}+hkb_{12}+hlb_{13}+klb_{23})\}$. Standard deviations of the last digit are in parentheses. There are two entries for each atom; the first are the parameters derived from data taken on a crystal in the colorless form at −110°C, the second from data taken on a crystal in the pink form at −110°C.

	x	y	z	b_{11}	b_{22}	b_{33}	b_{23}	b_{13}	b_{12}
C(1)	−1064 (2)	−3086 (2)	3080 (2)	71 (2)	62 (2)	44 (2)	55 (3)	63 (3)	75 (4)
	−1067 (3)	−3087 (3)	3077 (3)	88 (4)	99 (4)	68 (3)	99 (6)	108 (6)	115 (7)
C(2)	−1788 (2)	−2127 (2)	2651 (2)	73 (2)	67 (2)	58 (2)	74 (4)	77 (4)	82 (4)
	−1788 (3)	−2125 (3)	2651 (3)	83 (4)	105 (4)	76 (3)	110 (7)	106 (6)	112 (7)
C(3)	−3398 (2)	−2303 (2)	2772 (2)	82 (2)	93 (2)	69 (2)	91 (4)	90 (4)	120 (4)
	−3399 (3)	−2302 (3)	2773 (3)	88 (4)	132 (5)	86 (4)	115 (7)	112 (6)	142 (7)
C(4)	−3735 (2)	−3232 (2)	3895 (2)	81 (2)	109 (3)	72 (2)	99 (4)	104 (4)	109 (4)
	−3732 (3)	−3233 (4)	3898 (3)	90 (4)	147 (5)	93 (4)	135 (7)	132 (7)	147 (8)
C(5)	−3788 (2)	−5083 (2)	3349 (2)	100 (3)	89 (3)	87 (2)	116 (4)	128 (4)	96 (4)
	−3786 (3)	−5077 (4)	3354 (3)	103 (4)	130 (5)	107 (4)	156 (8)	150 (7)	125 (8)
C(6)	−1791 (2)	−4446 (2)	3765 (2)	110 (3)	93 (3)	79 (2)	124 (4)	128 (4)	137 (4)
	−1786 (3)	−4443 (3)	3770 (3)	112 (4)	136 (5)	98 (4)	165 (7)	151 (7)	166 (8)
C(1′)	989 (2)	−2223 (2)	1788 (2)	75 (2)	63 (2)	60 (2)	70 (4)	86 (4)	93 (4)
	985 (3)	−2227 (3)	1786 (3)	79 (3)	95 (4)	72 (3)	98 (6)	101 (6)	112 (7)
C(2′)	−556 (2)	−2936 (2)	117 (2)	75 (2)	73 (2)	61 (2)	74 (4)	84 (4)	95 (4)
	−553 (3)	−2939 (3)	119 (3)	88 (4)	104 (4)	76 (3)	106 (7)	110 (6)	117 (7)
C(3′)	−351 (2)	−2584 (2)	−1298 (2)	90 (2)	95 (3)	59 (2)	90 (4)	88 (4)	124 (4)
	−347 (3)	−2581 (3)	−1298 (3)	99 (4)	131 (5)	77 (3)	123 (7)	114 (6)	145 (8)
C(4′)	1833 (2)	−962 (2)	−491 (2)	104 (3)	93 (3)	80 (2)	121 (4)	125 (4)	129 (5)
	1837 (3)	−966 (3)	−491 (3)	101 (4)	126 (5)	87 (4)	135 (7)	126 (7)	135 (8)
C(5′)	3180 (2)	−1286 (2)	748 (2)	89 (2)	125 (3)	85 (2)	137 (4)	127 (4)	145 (5)
	3172 (3)	−1288 (4)	737 (3)	103 (4)	161 (5)	114 (4)	188 (8)	169 (7)	182 (8)
C(6′)	3108 (2)	−1079 (2)	2377 (2)	71 (2)	105 (3)	66 (2)	94 (4)	80 (4)	106 (4)
	3107 (3)	−1076 (3)	2376 (3)	86 (4)	145 (5)	89 (4)	141 (7)	119 (7)	143 (8)
C(7)	675 (2)	−2689 (2)	3108 (2)	76 (2)	56 (2)	52 (2)	54 (4)	67 (4)	84 (4)
	676 (3)	−2685 (3)	3109 (3)	84 (4)	88 (4)	63 (3)	81 (6)	87 (6)	105 (7)
O(8)	1865 (1)	−2743 (1)	4254 (1)	101 (2)	122 (2)	76 (2)	137 (3)	105 (3)	165 (4)
	1866 (2)	−2742 (3)	4254 (2)	103 (3)	161 (4)	92 (3)	167 (6)	122 (5)	182 (6)

this problem by refinement of disordered half-atoms were unsatisfactory. Since it was clear that these atoms in the cyclohexenyl rings were relatively free to vibrate thermally or exist in two stable half-chair conformations [one conformation having C(4′) up and C(5′) down relative to the plane of the ring, the other conformation being the opposite] we decided to retake the data at low temperature in order possibly to isolate one favored conformation. The refined parameters from the room-temperature data were used in the refinement of the low-temperature data. As mentioned above, data were also collected at low temperature on a crystal in the pink form. This data set was also refined independently, using as starting parameters those obtained from the room-temperature data. Refinement continued on both low-temperature data sets until shifts in the parameters were less than $\frac{1}{3}$ of their standard deviation. No disorder was seen in the cyclohexene rings at low temperature. The final R values were 0·051 for the low-temperature colorless form data and 0·058 for the pink form low-temperature data. The final difference Fourier maps showed no significant residual peaks (greater than 0·3 e Å^{-3}). The average $w_f\Delta F^2$ were independent of F_o and $\sin\theta/\lambda$ validating the weighting scheme used in the refinement.

The atomic scattering factors for carbon and oxygen are from *International Tables for X-ray Crystallography* (1962). The scattering factors for the hydrogen atoms were from Stewart, Davidson & Simpson (1965). The final atomic parameters for the low temperature forms are in Tables 2 and 3.*

Results

A stereo view of the molecule is given in Fig. 1. The bond distances and angles obtained from refinement of the data collected at low temperature on a crystal in the colorless form are shown in Figs. 2 and 3. A half-normal probability plot (Abrahams & Keve, 1971) was constructed from the positional parameters, to compare the results obtained from refinement of the data set collected on the colorless form and the pink form of DCK at low temperatures. This plot, which includes only the non-hydrogen positional parameters, is shown in Fig. 4. The parameter with the largest observed difference in the two forms and also showing the largest deviation from the expected straight line of Fig 4 is the z coordinate of C(5′) which lies about five standard deviations from the best straight line through all points. This is an atom which is disordered at room temperature. The remainder of the positional parameters appear to have a linear relation in the half-normal probability plot, giving a slope of 1·01 (standard deviation 0·04) validating the weighting scheme employed,

Table 3. *Hydrogen atom parameters* (*coordinates* × 10^3)

Standard deviations of last digit are in parentheses.

	x	y	z	B_{iso}
H(C2)1	−121 (2)	−119 (2)	227(2)	1·7 (3) Å^2
	−125 (4)	−122 (4)	226 (4)	1·6 (5)
H(C3)1	−463 (2)	−314 (2)	155 (2)	2·2 (3)
	−462 (4)	−315 (5)	152 (4)	2·2 (5)
H(C3)2	−305 (2)	−93 (2)	330 (2)	2·1 (3)
	−310 (5)	−90 (5)	326 (4)	2·8 (6)
H(C4)1	−499 (3)	−362 (3)	375 (3)	3·1 (4)
	−494 (4)	−357 (4)	379 (4)	2·3 (6)
H(C4)2	−259 (2)	−216 (2)	519 (2)	1·8 (3)
	−259 (4)	−211 (4)	525 (4)	1·7 (5)
H(C5)1	−485 (2)	−611 (2)	202 (2)	2·5 (3)
	−488 (5)	−609 (5)	199 (4)	2·5 (6)
H(C5)2	−410 (3)	−577(3)	399 (2)	2·8 (4)
	−409 (5)	−573 (5)	399 (4)	2·5 (6)
H(C6)1	−192 (2)	−565 (2)	317 (2)	2·0 (3)
	−189 (5)	−572 (5)	321 (5)	3·4 (7)
H(C6)2	−78 (2)	−370 (2)	510 (2)	1·8 (3)
	−75 (4)	−366 (4)	515 (4)	2·1 (5)
H(C2′)1	−191 (2)	−381 (2)	−24 (2)	2·0 (3)
	−193 (4)	−382 (4)	−25 (4)	1·7 (5)
H(C3′)1	−117 (2)	−224 (2)	−187 (2)	2·1 (3)
	−123 (5)	−221 (5)	−190 (5)	3·5 (7)
H(C3′)2	−94 (3)	−392 (2)	−236 (2)	2·1 (3)
	−101 (5)	−397 (5)	−238 (4)	2·3 (6)
H(C4′)1	193 (2)	−102 (2)	−153 (2)	2·1 (3)
	193 (5)	−101 (5)	−156 (5)	3·2 (7)
H(C4′)2	226 (3)	44 (3)	28 (2)	2·4 (3)
	229 (5)	46 (5)	28 (5)	3·1 (7)
H(C5′)1	268 (3)	−272 (3)	1 (3)	2·4 (3)
	267 (5)	−277 (5)	−2 (4)	2·6 (6)
H(C5′)2	459 (3)	−23 (3)	126 (3)	2·4 (3)
	461 (5)	−27 (5)	125 (5)	3·0 (6)
H(C6′)1	367 (3)	−163 (2)	298 (2)	2·4 (3)
	367 (5)	−161 (5)	298 (4)	2·6 (6)
H(C6′)2	392 (2)	35 (2)	330 (2)	2·1 (3)
	393 (5)	40 (5)	333 (5)	2·8 (6)

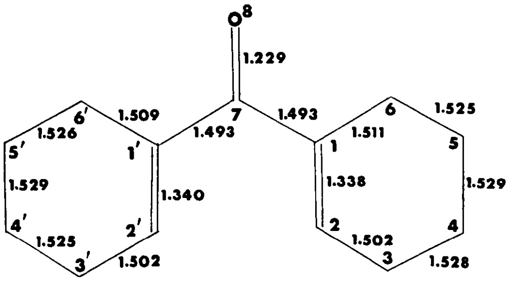

Fig. 2. Numbering scheme and bond distances in Å. Standard deviation for all distances is 0·002 Å.

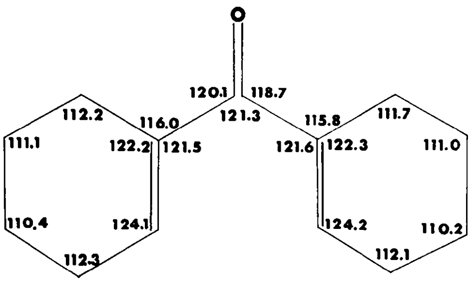

Fig. 3. Bond angles (°). Standard deviations of angles are 0·1°.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30915 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

and an intercept of −0·005. The anisotropic temperature-factor parameters of the pink form appear to be increased, relative to those of the colorless form, by an average of about 20% for all carbon and oxygen atoms. In general the same results are seen for the hydrogen-atom parameters. Since it is doubtful if a significant difference is observed between the colorless and pink forms, all calculated results (distances and angles) shown are from the refined coordinates of the colorless form data. No data are included here for the room-temperature data set.

The bond lengths and angles are in good agreement with accepted values. The distances and angles in the cyclohexene rings compare well with values found in 4-diethylcarbamoyl-1-cyclohexene-5-carboxylic acid (Pedone, Benedetti, Immirzi & Allegra, 1969). The distances and angles in cyclohexene ring C(1)–C(6) are consistent with the values found in ring C(1′)–C(6′). The carbon–hydrogen bond distances vary between 0·96 and 1·01 Å.

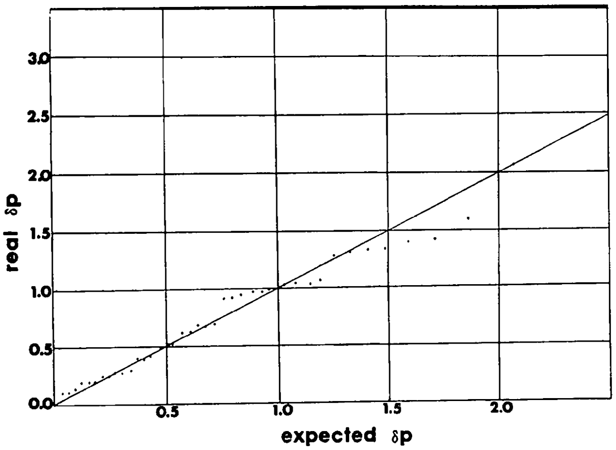

Fig. 4. Half-normal probability plot (Abrahams & Keve, 1971) comparing the final positional parameters of the non-hydrogen atoms as obtained from refinement of the colorless and pink crystal forms.

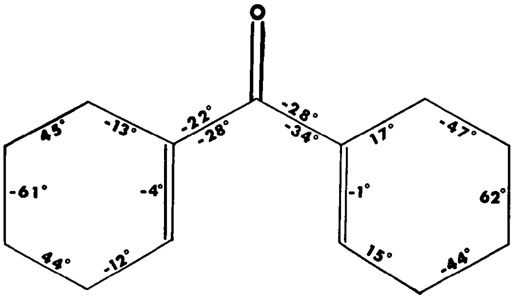

Fig. 5. Conformational angles in DCK. *cis* conformation is taken as 0°. Rotation in the right-handed sense is given in degrees.

Perhaps the most interesting results are seen in the conformational angles (Fig. 5). Rotations around the C(1)–C(7) and C(1′)–C(7) bonds of 34 and 28° respectively cause the cyclohexene rings to be tilted with respect to the plane of the carbonyl group [C(1)–C(7)–O(8)–C(1′)] in opposite directions as can be seen by a view down the O(8)–C(7) bond (Fig. 6). This nonplanarity results from steric hindrance between H(C2) and H(C2′). Analogous effects have been observed for benzophenone and its derivatives (Rekker & Nauta, 1954). Pattabhi & Venkatesan (1973) determined the rotation for each of the benzene rings away from planarity to be 28° in 3,3′-dibromobenzophenone. Pattabhi & Venkatesan have also calculated, by semi-empirical energy minimization methods, theoretical values for these twists to be 42–45° for the isolated benzophenone and 30° for the molecule 3,3′-dibromobenzophenone in the crystal form. The contact between H(C2) and H(C2′) is shown in Fig. 7 to be 2·41 Å, which is near the sum of the van der Waals radii of two hydrogen atoms, 2·4 Å (Pauling, 1960). The crowding between H(C2) and H(C2′) causes the cyclohexene rings to be tilted in such a manner that disrotatory closure across C(2)–C(2′) would be difficult without the systems first becoming more planar. The rings are in a favorable relation, however, for conrotatory closure.

Bucourt (1964) has calculated the internal dihedral angles for cyclohexene by energy-minimization techniques. These theoretical values and the experimental values of Pedone, Benedetti, Imirzi & Allegra (1969) are virtually identical to the torsion angles found in the cyclohexene rings of DCK and illustrated in Fig. 5. The tilting of the plane of C(2)–C(1)–C(6) from the plane of the carbonyl group is approximately related to the tilt of C(2′)–C(1′)–C(6′) by a twofold axis through C(7)–O(8). This can be seen in Fig. 6 and in the identity of the signs of the torsion angles around C(7)–C(1) and C(7)–C(1′). The potential twofold symmetry of the DCK molecule is destroyed, however, by the internal conformation of the cyclohexene rings, as shown by the fact that the signs of the angles in each ring are opposite, which indicates that the internal conformations of the rings are related by a mirror plane through C(7)–O(8) perpendicular to the rings.

The result of this difference in conformation of the

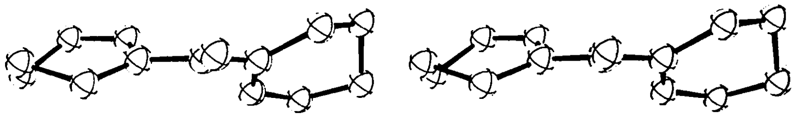

Fig. 6. Stereo view of DCK as viewed down O(8)–C(7) bond, showing twist of rings.

cyclohexene rings relative to the oxygen is that the torsion around the bond C(1′)–C(6′) causes H(C6′)1 to be moved closer to O(8) and H(C6′)2 farther away. If the internal conformation of the cyclohexene rings had been related by a twofold axis the hydrogens on C(6′) would have been equidistant from O(8), as are H(C6)1 and H(C6)2. At room temperature the ring C(1′)–C(6′) [and to a lesser extent ring C(1)–C(6)] is disordered at C(4) and C(5), indicating that for each ring both conformations are present. As is shown in Fig. 7, at low temperature H(C6′)1 has a contact of 2·44 Å with O(8) and the C–H–O bond angle is 103°. Therefore, H(C6′)1 is in an excellent position for hydrogen abstraction by O(8) and, being in an allylic position, is acidic in character. The transfer of H(C6′)1 to O(8) would result in a delocalized zwitterion or diradical which could cyclize in solution, but could not in the crystal lattice owing to the tightness of the crystal packing.

Another interesting contact, in this case intermolecular, exists between C(3′) and H(C3′)2 with O(8) of a molecule translated +1 unit in the **b** direction and inverted by a center of symmetry. The hydrogen–oxygen distance is 2·48 Å and the C–H–O angle is close to 180°. The H(C3′)2 is also allylic and therefore acidic in character and it is consequently just as possible that an intermolecular transfer of hydrogen occurs, yielding a different diradical. There is, however, no indication from the present results that the C=O distance is increased in the pink form [colorless form: 1·229 (2) Å, pink form: 1·231 (3) Å]. This is in agreement with the lack of difference observed in the half-normal probability plot. We therefore have to conclude that the color change is partial, probably occurring only at the surface, and that the increase in apparent thermal motion of the pink form is due to the shock of heating the crystal during irradiation and returning it to the cold stream.

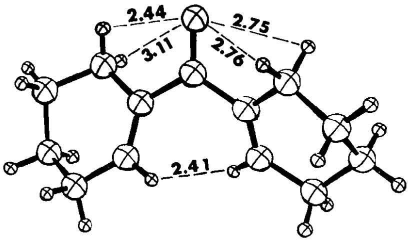

Fig. 7. Drawing of the molecule including the hydrogen atoms. Atoms with a close intramolecular contact are connected by a dashed line. The distance in Å is given.

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