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THE CRYSTAL AND MOLECULAR STRUCTURE AND CIRCULAR DICHROISM SPECTRA OF (-)-2,3-BORNANEDIONE α- AND β-HYDRAZONES

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Abstract—The structures of the α- and β-hydrazones of (-)-bornane-2,3-dione, $C_{10}H_{16}N_2O$, were confirmed as the 3*E* and 3*Z* geometric isomers, respectively, from 3-dimensional counter data. Both crystallize in the orthorhombic space group $P2_12_12_1$ with $Z = 4$. Cell dimensions are 6.832(1), 11.526(3), 12.883(2) Å for the α-isomer and 7.313(1), 11.214(2), 12.681(1) Å for the β-isomer. Both were solved by direct methods and refined by full matrix least squares. In contrast to 2,3-bornanedione, which has an unusually long (1.540 Å) $sp^2C(2)$-$sp^2C(3)$ bond length, the hydrazones have a more normal C(2)-C(3) bond length (1.469 Å). There is intermolecular N-H ... N H-bonding in the crystals of both the α- and β-hydrazones; in the β-isomer there is also clearly an intramolecular N-H ... O=C H-bond. For each isomer there is a small right-handed skew sense (α +4.5°, β +2.5°) to the torsion angle formed about O=C-C=N. Both isomers exhibit (-) Cotton effects near 350 nm in their circular dichroism spectra in a KBr matrix or in dioxane solution, but become (+) in n-heptane. Analysis of the ^{13}C-NMR spectra of the α- and β-hydrazones is discussed.

The monohydrazones of camphorquinone (2,3-bornanedione) were first prepared and investigated many years ago.[2] It was found that a nearly 75% yield of hydrazone crystallized after 3 hr from a 1:1 mixture of camphorquinone and hydrazine in ethanol kept at 40°. This crystalline hydrazone (labelled α)[2] melted with gas evolution at 206° to give camphor. From the mother liquors, an isomeric hydrazone (called β)[2] steam distilled. It melted at 102°; continued heating to 150–160° caused resolidification and conversion to the α-isomer. On the basis of these data and similar findings with camphorquinone semicarbazones, it was concluded that the α- and β-hydrazones were stereoisomers.[2] The available evidence thus suggests that bornane-2,3-dione reacts exclusively at C-3 and that the α- and β-isomers are *E* and *Z*-isomers, with the steam volatile β-isomer probably possessing the *Z*(*syn*)-configuration. However, none of these suppositions were confirmed unambiguously prior to this work.

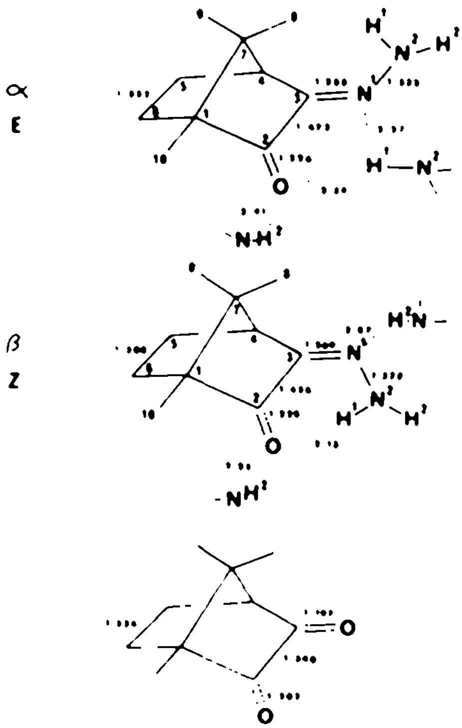


Fig 1. Structures of (-)-bornane-2,3-dione α-hydrazone (1) and β-hydrazone (2), and (-)-bornane-2,3-dione (bottom). Selected bond lengths are indicated on the structures. OH and NH distances are shown, however, only those less than 2.3 Å are believed to be involved in hydrogen bonding. A more complete set for 1 and 2 may be found in Tables 1; data for (-)-bornane-2,3-dione are obtained from reference 3.

Our interest in the hydrazones of camphorquinone is twofold: molecular structure and chiroptical properties, an unusually long sp^2C_2-sp^2C_3 bond length (1.540 Å) and a small (+0.1° to +2.9°) P-helicity skew angle.[3] The skew angle has been implicated as one of the criteria determining the sign of the long wavelength α-diketone CD Cotton effect (CE).[4] Since (-)-camphorquinone exhibits differently signed long wavelength CD CE's in solution [(-)-CE] and the solid phase [(+)-CE][4] it was particularly interesting to learn whether the hydrazones exhibit a similar behaviour. We therefore initiated a structure-spectroscopic investigation of the α- and β-hydrazones of (-)-camphorquinone, (1 and 2) respectively. In what follows we describe their crystallographic structure determinations and CD spectra, with the latter measured in the solid state and in solvents of varying polarity.

RESULTS AND DISCUSSION

Molecular structure

ORTEP[5] drawings of the α- and β-hydrazones of (-)-camphorquinone are shown in Figs 2 and 3. The isomeric molecules are virtually identical except for the orientation of the terminal N atoms in the hydrazone group. Bond lengths (Fig 1) and angles are given in Table 1. For the most part these agree in the two compounds as well as with those found in other camphor

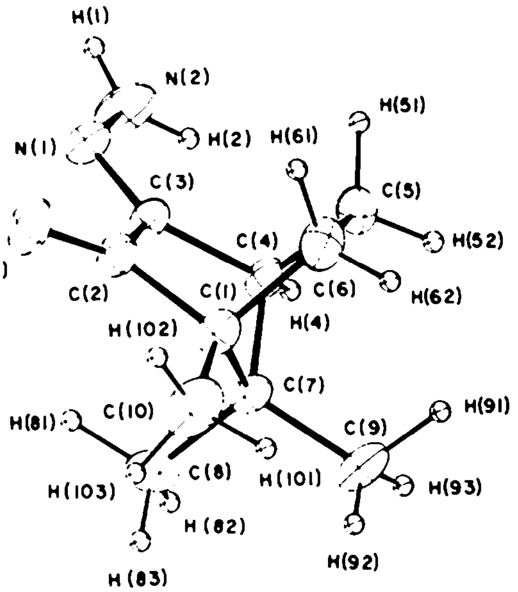


Fig. 2. ORTEP[5] drawing of α-hydrazone 1. The thermal ellipsoids are drawn for 50% probability, except for those of hydrogen atoms, which are not drawn to scale.

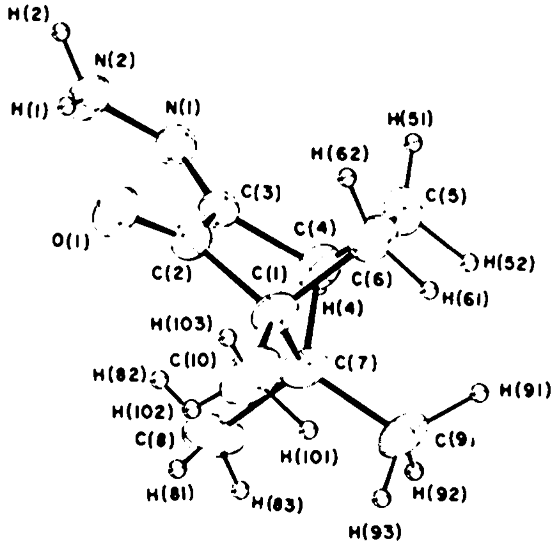


Fig. 3. ORTEP[5] drawing of β-hydrazone 2.

structures.[3,6–10] The difference between the C(5)-C(6) distances in the two compounds is not considered statistically significant. The estimated standard deviation for this bond length in the β-isomer is large. As might be expected, the major differences occur around C(2) and C(3). In 1 the N(1)-C(3)-C(4) angle is large (132.3°); whereas, in 2 it is the N(1)-C(3)-C(2) angle that is large (130.5°). This may in part be due to steric effects, since a large N(1)-C(3)-C(2) angle would tend to increase the separation between the terminal NH_2 group and the O atom. Such effects would be more important in the β-isomer (2). The C(3)-N(1)-N(2) angle is also slightly larger in the β-isomer.

The C(2)-C(3) bond length in the two compounds averages 1.464(8) Å, approximately that expected for a single bond between two sp^2 C atoms. In the structure of camphorquinone,[3] this bond length is unusually long, averaging 1.540 Å for the two molecules in the asymmetric unit.

There has been a considerable interest in the electronic and CD spectra of α-substituted camphor derivatives, particularly α-diketone systems.[4] In those systems, evidence points to a C2 symmetry due to out of plane skewing of the substituents.[3] For hydrazones 1 and 2 this can best be represented by considering the torsion angle N(1)-C(3)-C(2)-O(1), corresponding to the interplanar angles between the planes defined by N(1), C(3), C(2) and C(3), C(2), O(1). The angle is +4.1 and +2.5° in 1 and 2 respectively, both corresponding to a right-handed P-helicity skew sense. Another torsion angle of interest is that between the planes defined by N(1), N(2), C(3) and N(1), C(2), C(3). This angle is +176.1 and −3.3° in 1 and 2 respectively.

Angles between least-squares planes of interest are given in Table 2. These angles agree with those found in other camphor structures.[3,6–10] Calculations show that the atoms defining each of the three four-atom planes lie approximately in that plane.

Table 1(a). Bond distances (in Å) for non-hydrogen atoms[a]

Atoms	α-Isomer	β-Isomer
O(1)-C(2)	1.226(4)Å	1.228(8)Å
N(1)-N(2)	1.332(4)	1.328(7)
N(1)-N(3)	1.288(3)	1.269(8)
C(1)-C(2)	1.516(4)	1.508(8)
C(1)-C(6)	1.556(4)	1.588(10)
C(1)-C(7)	1.556(4)	1.576(9)
C(1)-C(10)	1.508(4)	1.505(9)
C(2)-C(3)	1.472(4)	1.456(9)
C(3)-C(4)	1.503(4)	1.521(9)
C(4)-C(5)	1.538(4)	1.549(11)
C(4)-C(7)	1.546(4)	1.531(9)
C(5)-C(6)	1.552(5)	1.508(14)
C(7)-C(8)	1.521(5)	1.529(9)
C(7)-C(9)	1.526(4)	1.528(9)

Table 1(b). Bond angles (in deg) for non-hydrogen atoms

Atoms	α-Isomer	β-Isomer
N(2)-N(1)-C(3)	118.3(3)[a]	120.4(5)[a]
C(2)-C(1)-C(6)	103.5(2)	102.5(5)
C(2)-C(1)-C(7)	100.5(2)	100.2(5)
C(2)-C(1)-C(10)	115.6(2)	116.7(6)
C(6)-C(1)-C(7)	101.6(2)	99.5(6)
C(6)-C(1)-C(10)	114.8(3)	114.4(6)
C(7)-C(1)-C(10)	118.5(2)	120.5(5)
C(1)-C(2)-O(1)	127.4(3)	125.6(6)
C(3)-C(2)-O(1)	127.9(3)	127.4(5)
C(1)-C(2)-C(3)	104.7(2)	107.0(5)
N(1)-C(3)-C(2)	121.4(2)	130.5(5)
N(1)-C(3)-C(4)	132.3(3)	124.8(5)
C(2)-C(3)-C(4)	106.1(2)	104.6(5)
C(3)-C(4)-C(5)	105.0(2)	104.9(6)
C(3)-C(4)-C(7)	101.0(2)	102.1(5)
C(5)-C(4)-C(7)	102.5(2)	102.1(5)
C(4)-C(5)-C(6)	102.5(2)	103.4(6)
C(1)-C(6)-C(5)	104.5(2)	105.1(6)
C(1)-C(7)-C(4)	94.3(2)	94.4(5)
C(1)-C(7)-C(8)	112.8(3)	111.1(6)
C(1)-C(7)-C(9)	114.1(3)	114.0(6)
C(4)-C(7)-C(8)	113.0(2)	114.6(6)
C(4)-C(7)-C(9)	113.5(2)	113.2(6)
C(8)-C(7)-C(9)	108.7(2)	109.0(5)

[a] The figures in parentheses are the standard deviations of the least significant here and throughout this paper.

Table 2. Angles (in deg) between least-squares planes[a]

Plane 1: C(1), C(4), C(7)

1 $-2.120x + 10.259y - 4.301z = 8.038$

2 $2.809x + 9.902y - 3.425z = 5.094$

Plane 2: C(1), C(2), C(3), C(4)

1 $-0.336x + 9.679y + 6.967z = 10.401$

2 $0.965x + 8.988y + 7.396z = 11.616$

Plane 3: C(1), C(4), C(5), C(6)

1 $2.024x - 2.237y + 12.048z = 1.060$

2 $-2.266x - 2.428y + 11.740z = 6.050$

Plane 4: C(2), C(3), C(5), C(6)

1 $1.011x + 4.425y + 11.742z = 7.769$

2 $-0.811x + 3.866y + 11.820z = 9.935$

1:	(1)-(2)	54.4	(1)-(3)	125.2	(1)-(4)	90.5
	(2)-(3)	70.9	(2)-(4)	36.1	(3)-(4)	34.8
2:	(1)-(2)	53.1	(1)-(3)	124.1	(1)-(4)	89.4
	(2)-(3)	71.0	(2)-(4)	36.4	3)-(4)	34.6

[a] All planes are unweighted. x,y, and z are in orthorhombic fractional coordinates.

Table 3. Intermolecular contacts $\geq$ 3.5 Å[a]

	α-Isomer (1)	β-Isomer (2)
N(1)· · ·O(1)^{I}	-----	3.475
N(2)· · ·O(1)^{II}	3.216	-----
N(2)· · ·O(1)^{I}	3.293	2.961
N(2)· · ·N(1)^{I}	3.043	-----
N(2)· · ·N(1)^{III}	-----	3.112

[a] A dash indicates this distance is greater than 3.5 Å. Roman numeral subscripts denote the following equivalent positions relative to the reference molecule at x, y, z.

I -0.5 + x, 1.5 - y, 1 - z

II - 1 + x, y, z

III 0.5 + x, 1.5 - y, 1 - z

There is H-bonding in both isomers. Intermolecular contacts ≤3.5 Å are given in Table 3. Because of the different positions of the terminal NH_2 groups of the hydrazone, the H-bonding is different in the two compounds. For both isomers, molecules are linked by H-bonds roughly parallel to the *a* axis. In the α-isomer an H bond is found between N(2)-H(1) · · · N(1)^{I}. (Table 3 for meaning of superscripts.) The H(1)-N(1)^{I} distance is 2.27 Å. In the β-isomer there is quite clearly an *intramolecular H-bond*, N(2)-H(1) · · · O(1). Atom H(1) is in a position which brings it to a minimum contact distance with O(1) (2.13 Å). There is also a N(2)-H(2) · · · O(1)^{II} intermolecular H-bond. In this the H(2)-O(1) distance is 2.25 Å.

Computer generated [11] packing diagrams are shown in Figs. 4 and 5. H-bonds are indicated by dashed lines. Other than these H-bonded contacts, none of the other short intermolecular contacts in Table 3, all of which involve N(1), N(2) or O(1) is believed to indicate H-bonding or to have any important effect on the packing or crystal structure.

NMR and structure

^{13}C-NMR data for 1 and 2 are presented in Table 4. The only significant differences in C resonances were displayed by C-3 and C-4. The +6.08 ppm resonance difference ($\Delta\delta = \delta(1) - \delta(2)$ seen for C-3 can *not* be explained as a simple *syn* + *anti* change. This was

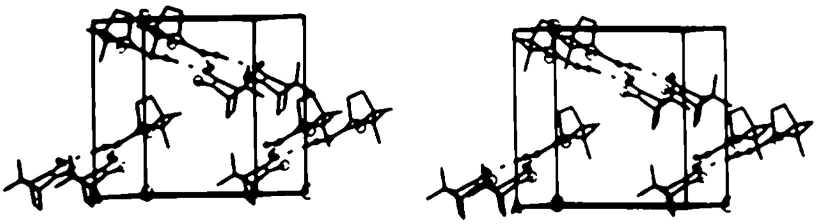


Fig. 4. Computer-generated packing diagram for α-hydrazone 1. Hydrogen bonds are indicated by dashed lines. Small circles denote nitrogen atoms; large circles denote oxygen atoms.

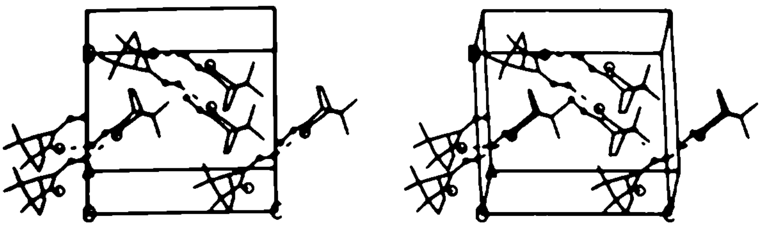
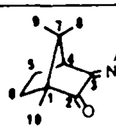
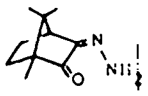
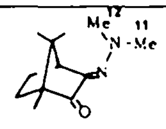
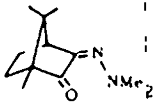


Fig. 5. Computer-generated packing diagram for β-hydrazone 2. Hydrogen bonds are indicated by dashed lines. Small circles denote nitrogen atoms; large circles denote oxygen atoms.

Table 4. ^{13}C-NMR chemical shifts[a], assignments and differences (Δδ) for hydrazones of camphorquinone

Carbon Number[b]	 1	 2	Δδ	 anti	 syn	Δδ
1	57.98 (s)	58.15 (s)	-0.17	56.22 (s)	59.62 (s)	-3.40
2	204.52 (s)	203.59 (s)	+0.93	204.00 (s)	196.89 (s)	+7.11
3	150.35 (s)	144.27 (s)	+6.08	143.80 (s)	142.71 (s)	+1.09
4	44.87 (d)	50.35 (d)	-5.48	50.78 (d)	53.66 (s)	-2.79
5	23.52 (t)	25.68 (t)	-2.16	25.56 (t)	26.17 (t)	-0.61
6	31.36 (t)	30.19 (t)	+1.17	30.01 (t)	30.30 (t)	-0.29
7	45.63 (s)	46.97 (s)	-1.34	45.34 (s)	45.57 (s)	-0.23
8	18.02 (q)	18.49 (q)	-0.47	20.36 (q)	19.88 (q)	+0.48
9	20.42 (q)	20.42 (q)	0.00	17.90 (q)	18.36 (q)	-0.46
10	9.01 (q)	8.72 (q)	+0.29	8.83 (q)	9.25 (q)	-0.42
11	-----	-----	-----	45.75 (q)	48.18 (q)	-2.43
12	-----	-----	-----	45.75 (q)	48.18 (q)	-2.43

[a] Measured in $CDCl_3$ at 25.0 MHz, calibrated vs $CDCl_3$ (77.05 ppm) and reported in ppm downfield from TMS.

[b] Conventional numbering system.

[c] N,N-Dimethylhydrazones were prepared by reaction of (-)-camphorquinone with N,N-dimethylhydrazine. The dimethylhydrazone was isolated as a viscous oil containing a ca 2:1 mixture of *anti*:*syn* isomers (determined by NMR) Warming the mixture in $CDCl_3$ to ca 60° caused the *syn* isomer to convert almost entirely to *anti*.

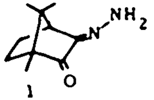
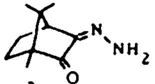
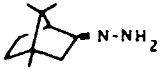
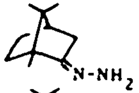
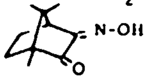
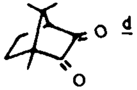
deduced from the reported C-2 resonances[12] of the *syn* and *anti* oximes of bicyclo[2.2.1]heptan-2-one, resonances which occur at 167.4 ppm and 166.3 ppm and yield only a 1.1 ppm resonance difference. We attribute the large Δδ(= +6.08) for C-3 to a lessening of the stereoelectronic demand on C-3 by C-2 in **2** due to intramolecular H-bonding, which is present in **2**, but not in **1**. That this is reasonable can be inferred from ^{13}C-NMR data for the *syn* and *anti* N,N-dimethylhydrazones of camphorquinone (Table 4), which showed a Δδ for C-3 of only 1.1 ppm. The −5.48 ppm Δδ for C-4 of **1** and **2** (Table 4) is attributed to a γ-gauche shielding effect in **1** due to the steric crowding of C-4 by the $-NH_2$ group. A similar, but slightly smaller effect is seen in the corresponding N,N-dimethylhydrazones.

The ^{1}H-NMR spectrum of pure **1** at 100 MHz in $CDCl_3$ at 38° showed three singlets (9H: 0.86, 1.00 and 1.02 ppm), which were assigned to the three Me groups; a multiplet (4H: 1.2–2.2 ppm); a doublet (1H: 2.80 ppm, J = 3.7 Hz), which was assigned to H-4 and a broad singlet at 6.35 ppm (intermolecular H-bonding). Upon heating the NMR sample to 50° for a few minutes, the spectrum of **1** displayed three new peaks, which persisted after cooling the NMR tube to 30°. These three new peaks appeared as two singlets (0.94 and 0.97 ppm) and a doublet (2.48 ppm, J = 3.7 Hz) and were attributed to the presence of the β-hydrazone (**2**). This assignment was confirmed by examining the ^{1}H-NMR spectrum of pure **2** at 100 MHz in $CDCl_3$ at 34°, a spectrum which showed three singlets (9H: 0.86, 0.94, 0.97 ppm) assigned to the three Me groups, a multiplet (4H: 1.2–2.2 ppm), a doublet (1H: 2.48 ppm, J = 3.7 Hz) which was assigned to H-4 and a broad singlet at 7.95 ppm (intramolecular H-bonding). The ratio of **1**:**2** was *ca.* 2:1 in the heated NMR tube, again confirming that **1** is more stable thermodynamically. The same equilibration rates could be seen in the ^{13}C-NMR spectrum as well. A 3:1 mixture of **1**:**2** was exhibited in the ^{13}C-NMR spectrum at 50° after 16 hr of data accumulation.

Chiroptical properties

The absolute configurations of hydrazones **1** and **2** may be traced to that of (+)-camphor,[13] from which their precursor, (-)-bornane-2,3-dione, was prepared by SeO_2 oxidation.[14] CD data for the α-hydrazone (**1**) and β-hydrazone (**2**) may be found in Table 5 and in Fig. 6. Unlike (-)-camphorquinone[4] (Table 5), for which much experimental and theoretical work has been done relating the CE sign of its long wavelength transition to dione skew angle and other features, the long wavelength CE's of **1** and **2** are both negative. It would appear, therefore, that the CE sign for the long wavelength transitions of hydrazones **1** and **2**, CD run in the solid phase, cannot be related directly to the absolute helicity (**P**) of the chromophore, helicity determined by X-ray crystallography. However, consistent with the CD studies of (-)-camphorquinone,[4] the hydrocarbon solution CD spectra of **1** and **2** exhibit long wavelength CE's opposite in sign to those in the solid phase CD spectra. Interestingly, there is also a pronounced solvent effect on the long wavelength CE signs of **1** and **2** (*cf* Fig. 6 and Table 5) but not on the shorter wavelength transitions, whose CE signs remain solvent invariant. A similar solvent-dependent long wavelength CE sign change occurs with the hydrazones of both (-)-epicamphor and (+)-camphor. It is presently unclear whether the observed solvent-induced changes are due to orientation effects about the N–N bond. Presumably, the β-hydrazone (**2**) with its intramolecular N–H. . . . O=C H-bond should be less susceptible to solvent-induced reorientation about

Table 5. Circular dichroism and UV spectral data for hydrazones of (-)-camphorquinone, (+)-camphor and (-)-epicamphor $\lambda^{a}_{max}(\Delta\epsilon)$, $\lambda^{a}_{max}(\epsilon)$

Compound	n-Heptane	CF_3CH_2OH	KBr[b]
 1	365^{sh} (+0.23), 340^{sh} (47) 260^{sh} (+2.9), 263 (7470) 238 (+6.7), 248^{sh} (6270) 213 (-3.2)	343 (-0.39), 330^{sh} (4500) 276 (+8.3), 284 (13,000) 244^{sh} (6,600) 217 (-5.4)	368 (-4.0)
 2	382 (+0.37), 377 (314) 292 (+5.6), 293 (10,050) 239 (+1.5) 213 (-7.4)	367 (+0.33), 364 (280) 290 (+4.8), 292 (6700) 246 (+2.6) 216 (-13.1)	394 (-0.32) 346 (-0.38) 267 (+0.41)
	222 (+6.7), 228 (4880)	230 (-2.2), 226 (2880) 207 (10.73), 205 (4320)	
	228 (-3.8) 228 (4280) 210 (7950)	230 (+5.7), 228 (993) 213 (-1.8), 203 (3680)	
		335 (+0.42)[c] 335 (39)[c] 243 (+7.3)[c]	
 d	483 (-0.48), 484 (36)[e] 293 (+0.36), 280 (24) 234 (-0.91)	456 (-0.44), 454 (300) 285 (+0.41), 272^{sh} (480) 249 (-0.44), 250 (800)[f]	468 (+0.18) 308 (+0.20)

[a] In nm.

[b] Best KBr disc from five preparations; all discs gave essentially the same results. The discs were prepared by compression in a KBr die at 16,000 lb in^{-2} following intimate mixing of the sample (ca 1.5 mg) and 200 mg of Harshaw spectrograde KBr powder (density KBr = 2.75 g cm^{-1} 25°C). This gave a translucent disc of 17 x 10^{-3} in. thickness (pathlength).

[c] Run in absolute ethanol. Data from ref 15.

[d] Data from ref. 4.

[e] Run in methylcyclohexane

[f] Not maximum

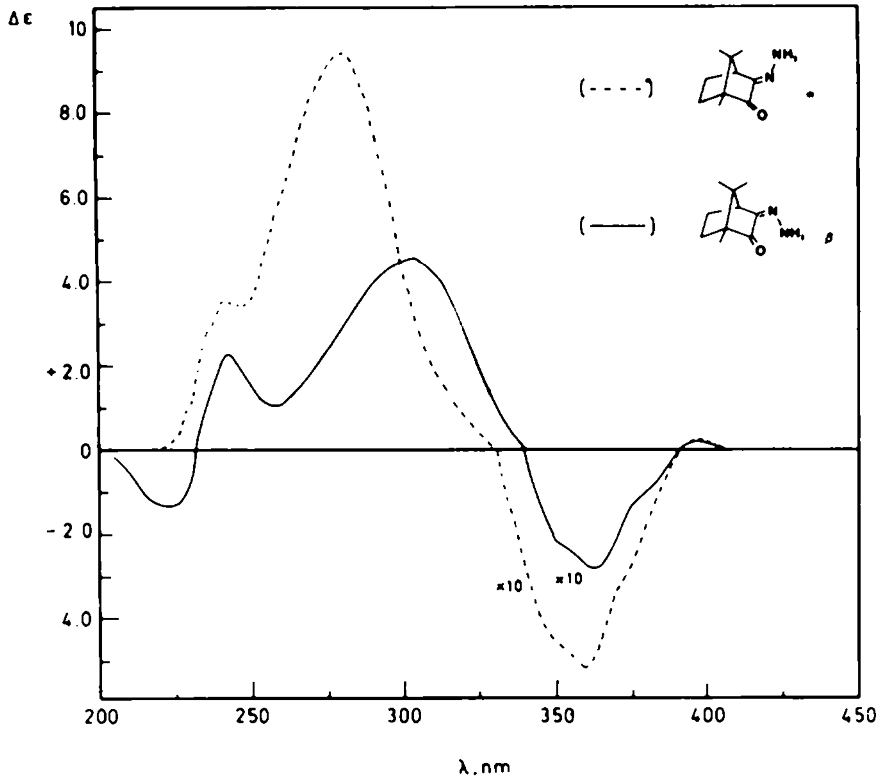


Fig. 6. Ciccular dichroism spectra of (-)-bornane-2,3-dione α-hydrazone (1) (——) and β-hydrazone (2) (-----) run in p-dioxane solvent at room temperature.

the N–N bond, nevertheless, the long wavelength CE signs of 2 do vary with changing solvent (*cf* Table 5 and Fig. 6).

It is premature to associate the observed chiroptical properties of the hydrazones of Table 5 with any specific structural features. We note one general feature of conjugated hydrazones of 1 and 2 and the conjugated oxime[15] of Table 5: the consistently positive CE's near 290 nm correlate well with the also consistently positive short wavelength ($\lambda \sim 230$ nm, R-band) CE's of α,β-unsaturated ketones derived from bicyclo[2.2.1] heptan-2-ones of the same absolute configuration.[16] Presumably, in all cases the CE sign-governing contributions to these bands are derived from ring-atom contributions, probably of the allylic axial type.[17] The exact assignment of the electronic transition giving rise to the relevant CD CE's of 1 and 2 is now known, but it is probably mainly of the $\pi \rightarrow \pi^*$ type, as has been suggested previously for the camphorquinone oxime of Table 5[17] and α,β-unsaturated ketones.[16]

CONCLUSIONS

The X-ray crystallographic structure of α-hydrazone (1) confirms the location of the hydrazone moiety and reveals its *anti* (*E*)-configuration (Fig. 2). Similarly, the location and configuration of the hydrazone in the β-isomer (2) are revealed as *syn* (*Z*)-(Fig. 3). The data also show interplanar torsion angles of +4.1° and +2.5°, for the C=O and C=N–N chromophores of 1 and 2 respectively. The CD spectra of 1 and 2 run in KBr discs show an inverse correlation of their long wavelength (-) CE signs with the P-helocity chromophore, unlike camphorquincne. Considerable variation with solvent is found in the CD spectra. The shorter wavelength CD transitions near 290 nm are consistently positive and appear to be determined by allylic axial groups (bonds).

EXPERIMENTAL

General. CD spectra were recorded on a JASCO J-40A instrument equipped with a photoelastic modulator. UV data were determined on a Cary 219 spectrophotometer. All rotations were determined in $CHCl_3$, unless otherwise indicated, on a Perkin-Elmer model 141 polarimeter. NMR spectra were measured on a JEOL FX-100 instrument in $CDCl_3$, unless otherwise indicated, and reported in δ (ppm) downfield from TMS. All m.p.s were determined on a Thomas–Hoover capillary apparatus and are uncorrected. Spectral data were obtained using spectral grade solvents.

(+)-2-3-*Bornane 3-hydrazone.* The α- and β-hydrazones were prepared by reaction of (-)-2,3-bornanedione, $[\alpha]_D^{23} = -108°$ (*c*0.67), with hydrazine followed by separation—all by the previously reported procedure.[2] The α-isomer was recrystallized from $CHCl_3$ to give white wedge-shaped crystals, m.p. 202–204° (dec) [lit.[2] m.p. 206°]; the β-isomer was recrystallized from *n*-hexane to give yellowish-white needles, m.p. 101–103° [lit.[2] m.p. 103°]. The pure α-hydrazone had $[\alpha]_D^{28} = +248.5°$ (*c*0.11), [lit[2] $[\alpha]_D = +287.4°$ (*c*1.2, $CHCl_3$]; UV and CD data in Table 5; and ^{1}H-NMR, δ: 0.86 (s, 3H), 1.00 (s, 3H), 1.02 (s, 3H), 1.2–2.2 (m, 4H), 2.80 (d, 1H, J = 3.7 Hz), 6.35 (br s, 1H) ppm; ^{13}C-NMR data in Table 4. The pure β-hydrazone had $[\alpha]_D^{28} = +96.19°$ (*c*0.10), [lit.[2] $[\alpha]_D = +231.3°$ (*c*1.2, $CHCl_3$)]; UV and CD data in Table 5; and ^{1}H-NMR, δ: 0.86 (s, 3H), 0.94 (s, 3H), 0.97 (s, 3H), 1.2–2.2 (m, 4H), 2.48 (d, 1H, J = 3.7 Hz), 7.95 (br s, 1H) ppm; ^{13}C-NMR data in Table 4.

Crystallographic studies

For crystallographic studies, crystals of the α-hydrazone (1) had prominent faces {010} bounded by {110} and {011}. The crystal chosen for intensity measurements was mounted on a glass fiber. Yellowish-white crystals of the β-isomer (2) were needles with the needle axis parallel to a, bounded by {010} and {110}. The crystal used for intensity measurements was a fragment cleaved from the end of one of these needles. The cleavage face could be approximated as {100}. The crystal was mounted in a glass capillary.

Crystal data for both compounds are listed in Table 6. Also listed are some of the experimental conditions used in the intensity measurements. The cell dimensions were obtained by minimizing the differences between observed and calculated setting angles for 25 reflections. Cu K_α (λ = 1.54178 Å) radiation, monochromatized by pyrolitic graphite was used throughout the study.

For both compounds, the choice of the space group was uniquely determined by the systematic absences.

All data were measured on an Enraf-Nonius CAD4 diffractometer at Brookhaven National Laboratory. The data in each case were collected by the θ-2θ scan method, the intensity scale being monitored by remeasuring a group of four reflections periodically. No evidence of crystal decomposition or machine instability was noted.

Absorption corrections were applied using a Gaussian integration method ($8 \times 8 \times 6$ and $8 \times 4 \times 6$ grids for 1 and 2 respectively). Equivalent reflections were averaged. Structure factors were calculated in the usual way, including correction for partial polarization of the incident beam due to the use of a monochromator.

Structure solution and refinement

The structures were both solved by use of the tangent refinement procedure, using the MULTAN package.[18] The program was allowed to choose its own origin defining reflections, enantiomorph defining reflection, and starting set, the last containing two general hkl reflections and one special reflection (phase limited to 0 or 180°). In each case the solution with highest combined figure of merit was used to generate an E-map from which the positions of all 13 non-H atoms could be determined.

Initial calculations were performed using programs described in the CRYSNET manual of Brookhaven National Laboratory.[19] The structures were refined using the CRYLSQ link of the XRAY72 system.[20] The atomic scattering factors for non-H atoms were the values of Cromer and Waber[21] and the atomic scattering factors for hydrogen were obtained from the calculations of Stewart *et al.*[22] No anomalous dispersion corrections were applied. The quantity minimized in least-squares calculations was $\Sigma w(|F_o| - |F_c|)^2$. There was no evidence of secondary extinction.

α-Isomer. Refinement of all non-H atoms with isotropic temp factors gave $R_1 = 0.14$. Conversion to anisotropic temp. factors followed by two cycles of full-matrix least squares refinement reduced R_1 to 0.09. A difference electron density synthesis gave acceptable positions for all of the H atoms. The H atoms were included in all subsequent refinements, but their positions and isotropic temp factors ($U = 0.050$) were not allowed to vary. For the final least-squares refinements, data were weighted by $1/\sigma_F^2$ where $\sigma_F = 0.600 - 0.015\,|F_o|$ for $F \leq 15.0$, and $\sigma_F = 0.358 + 0.0082\,|F_o|$ for $F > 15.0$. Least-squares refinement converged with $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$ equal to 0.052 and 0.060 respectively for 1128 reflections considered observed (i.e. having $I \geq 3\sigma_I$). The error in an observation of unit weight, defined as $(\Sigma(w|F_o| - |F_c|)^2/(N_o - N_v))^{1/2}$, where N_o is the number of observations and N_v is the number of variables, was 1.08.

β-Isomer. Isotropic refinement of all non-H atoms gave $R_1 = 0.17$. Conversion to anisotropic temp factors followed by two cycles of full-matrix least squares refinement reduced R_1 to 0.11. A difference electron density synthesis gave acceptable positions

Table 6. Crystal data and experimental conditions for isomers of (-)-2,3-bornane 3-hydrazone, $C_{10}H_{16}N_2O$

	α-Isomer (1)	β-Isomer (2)
a (Å)	6.832(1)	7.313(1)
b (Å)	11.526(3)	11.214(2)
c (Å)	12.883(2)	12.681(1)
Volume (Å^3)	1014	1040
D_c (g cm^{-3})	1.18	1.15
D_m (g cm^{-3})[a]	1.15(2)	1.12(2)
M (Daltons)	180.2	180.2
Z	4	4
Crystal Size (mm)	0.30 x 0.16 x 0.32 in direction of a, b, c respectively	0.43 x 0.31 x 0.13 in direction of a, b, c respectively
Systematic Absences	h00 (h odd) 0k0 (k odd) 00l (l odd)	Same
Space Group	$P2_12_12_1$	$P2_12_12_1$
μ (Cu K_α radiation) (cm^{-1})	13.60	13.25
Scan Rate (°/min)	0.83 to 3.33°	Same
Scan Range (°)	1.00 + 0.14 tan θ	Same
Max. sin θ/λ	0.63 (75° in θ)	Same
Reflections Measured	2595	2007
Total Unique Reflections	1236	1258
Reflections with $I > 3\sigma_I$	1128	843

[a] Measured by flotation in aqueous zinc nitrate solution.

Table 7. Fractional coordinates (× 10^4) for non-hydrogen atoms of 1 derived from the least-squares refinement

	x/a	y/b	z/c
O(1)	5633(3)	8497(2)	3408(2)
N(1)	1701(4)	7974(2)	4111(1)
N(2)	-170(4)	7820(3)	4365(2)
C(1)	3937(4)	9473(3)	1967(2)
C(2)	4124(4)	8757(2)	2949(2)
C(3)	2096(4)	8489(2)	3249(2)
C(4)	816(4)	9021(2)	2428(2)
C(5)	899(4)	10335(3)	2633(2)
C(6)	3050(5)	10637(3)	2357(3)
C(7)	2128(4)	8885(3)	1457(2)
C(8)	2494(6)	7624(3)	1168(2)
C(9)	1349(5)	9522(3)	505(2)
C(10)	5782(5)	9596(4)	1335(3)

Table 8. Fractional coordinates (× 10^4) for non-hydrogen atoms of 2 derived from the least-squares refinement

	x/a	y/b	z/c
O(1)	10173(6)	6455(4)	6514(4)
N(1)	6388(7)	7311(5)	5900(4)
N(2)	7597(8)	7732(5)	5213(4)
C(1)	8499(9)	5480(6)	7935(5)
C(2)	8725(9)	6253(5)	6971(5)
C(3)	6913(7)	6680(6)	6683(4)
C(4)	5647(9)	6141(6)	7507(5)
C(5)	5551(12)	4798(8)	7228(6)
C(6)	7447(14)	4354(6)	7481(6)
C(7)	6858(9)	6139(6)	8492(5)
C(8)	7428(11)	7376(7)	8875(5)
C(9)	6027(11)	5447(7)	9413(5)
C(10)	10209(11)	5184(8)	8541(6)

for ten of the sixteen H atoms. These atoms were included in the next refinement with fixed positions and temperatures factors ($U = 0.050$). After two cycles of least square refinement, R_1 was reduced to 0.08. A second difference Fourier synthesis gave reasonable positions for three of the remaining H atoms. These peaks appeared at reasonable distances from C(9), but the bond angles were unacceptable. Therefore the positions of these and the other three missing methyl H atoms were calculated. All sixteen H atoms were included in subsequent refinements with fixed positions and temp factors. For the final least-square refinements, data were weighted by $1/\sigma_F^2$ where $\sigma_F = 0.103 + 0.045\,|F_0|$ for $F \leq 30$, and $\sigma_F = 0.840 + 0.212\,|F_0|$ for $F > 30$. Least-square refinement converged with R_1 and R_2 equal to 0.072 and 0.085 respectively. The error in an observation of unit weight was 1.06 for 43 reflections with $I \geq 3\sigma_I$.

For both compounds refinement was terminated when the shifts in all parameters were less than one-half of their estimated standard deviations. Final difference Fourier maps showed only very small peaks of no physical significance. The final positional parameters for the non-H atoms are given in Tables 7 and 8. The thermal parameters for non-H atoms, the positional parameters for the H atoms, the root-mean-square components of thermal displacement along the principal axes of the thermal ellipsoids and the observed and calculated structure factors are available as supplementary material.

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