and **34** is considerably less than that predicted by the MNDO calculations and may not exist at all. In either case the *N*-methyl-*N*-acetylnitrenium ion **9** is expected to be unstable with respect to conversion to **34**. In the aromatic series the situation is slightly different, the conversion of **12b** to **37** ($\Delta H_f = 193.1$ kcal mol^{-1}) being much less exothermic. The reaction is therefore expected to be much less facile. However, as discussed above, our procedure does not allow a theoretical estimate of the activation barrier in this particular case. We also examined the conversion of **12b** to a species analogous to **33**, finding that such a structure did not represent a statble point on the MNDO potential surface.

Conclusion

The parent nitrenium ion **6** is a ground-state triplet. Substitution of the hydrogen atoms leads to considerable electron transfer to the nitrogen atom, especially in the aromatic series where the NH or $NCOCH_3$ group carries only ~20% of the positive charge. Electron transfer stabilizes both states approximately equally although the actual transfer of charge in the singlet is greater, the net result being a differential stabilization of the singlet which in the aromatic series falls below the triplet state.

The coefficients of the nonbonding orbital of the isoconjugate arylmethyl cations give a rough guide to the most reactive positions of the arylnitrenium ions toward simple nucleophiles. Detailed MNDO calculations give an apparently consistent picture of the same type of reactivity. Entropy effects appear to be unimportant in determining regioselectivity. Hydration energies must be taken into account if the order of reactivity of nucleophiles toward the nitrenium ions is to be predicted correctly. It is suggested that the calculated free energy for the formation of the nucleophile/nitrenium ion adduct be used as an indicator of relative reactivity.

Aryl nitrenium ions are not expected to undergo unimolecular decay at a significant rate. There is a high (>39 kcal mol^{-1}) barrier to rearrangement of the *N*-phenylnitrenium ion **12a** to the azepenium ion **28**. A quanternary isocyanate **37** is more stable than **12a**, but the limitations of the theoretical procedure prevent the estimation of the activation energy for this process.

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Appendix

Estimation of Hydration Energies (See Chart I). In the absence of parameters for *N*-acetylimines we replace the nitrogen atom by CH. Hydration energies calculated in this way will be too positive by an amount corresponding approximately to the hydrogen-bonding interaction between the imine-like nitrogen and the solvent. This error should, however, be considerably smaller than the difference between the hydration energies of benzene and pyridine (3.4 kcal mol^{-1}).

In the Hine and Mookerjee scheme, log γ is evaluated in terms of group contributions where γ is the activity coefficient in the ideal gas phase relative to infinitely dilute aqueous solution. The hydration energy of, for example, **22b** is calculated as follows. The individual contributions corresponding to the numbering scheme in I total 9.88. This is then converted to free energy and changed from the concentration-based standard used by Hine to that used here (cf. footnote *d* of Table IV). The determination for the oxonium ion **22a** proceeds similarly, using the log γ contribution for $OH_2^+(C)$ deduced before. In this case, since it is an ion, we add the contribution due to charging the cavity in which the molecule resides. This is calculated from eq 2 as described under Procedure.

Supplementary Material Available: Optimized Cartesian coordinates for all species studied in this report (35 pages). Ordering information is given on any current masthead page.

Charge-Transfer Band of 7-Norbornenone. Circular Dichroism of (1*R*)-2-Deuteriobicyclo[2.2.1]hept-2-en-7-one and (1*R*)-2-Methylbicyclo[2.2.1]hept-2-en-7-one

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Abstract: (1*R*)-[2-^{2}H]Bicyclo[2.2.1]hept-2-en-7-one (**1**), bicyclo[2.2.1]hept-2-en-7-one (7-norbornenone) (**2**), and (1*R*)-2-methylbicyclo[2.2.1]hept-2-en-7-one (**3**) were prepared from (1*R*)-7,7-dimethoxybicyclo[2.2.1]heptan-2-one *p*-toluenesulfonylhydrazone of known absolute configuration and optical purity. Circular dichroism spectra of deuterio ketone **1** ($\Delta\epsilon_{273}^{\max}$ −0.033, $\Delta\epsilon_{224}^{\max}$ −0.028, and $\Delta\epsilon_{213}^{\max}$ +0.029) and methyl ketone **3** ($\Delta\epsilon_{275}^{\max}$ −0.62, $\Delta\epsilon_{226}^{\max}$ +2.10, and $\Delta\epsilon_{208}^{\max}$ −3.0) confirm the existence of a new low-lying electronic transition near 225 nm whose existence and origin have been questioned during the past 20 years. The partial charge-transfer nature of this band is supported by preliminary calculations in the localized orbital random phase approximation.

7-Norbornenone (**2**) and its derivatives have been of interest to chemists for more than 20 years, with respect to both the phenomenon of neighboring group participation (or interaction)[2] and the existence and nature of a "mystery band" reportedly[3] occurring near 233 nm (ϵ 1290) in the ultraviolet (UV) absorption spectrum of **2**. This band was attributed to "a very unique transannular interaction between the non-conjugated double bond and the carbonyl group".[3] The 233-nm absorption band was shortly thereafter cited as evidence for an intermolecular charge-transfer $\pi \rightarrow \pi^*$ transition.[4-6] 7-Norbornenone also

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[2] (a) Winstein, S.; Shatavsky, M.; Norton, C.; Woodward, R. B. *J. Am. Chem. Soc.* **1955**, *77*, 4183-4184. (b) For a recent summary, see: Tanida, H. *Acc. Chem. Res.* **1968**, *1*, 239-245.

[3] Norton, C. J. Ph.D. Dissertation, Harvard University, 1955; pp 103, 122 ff.

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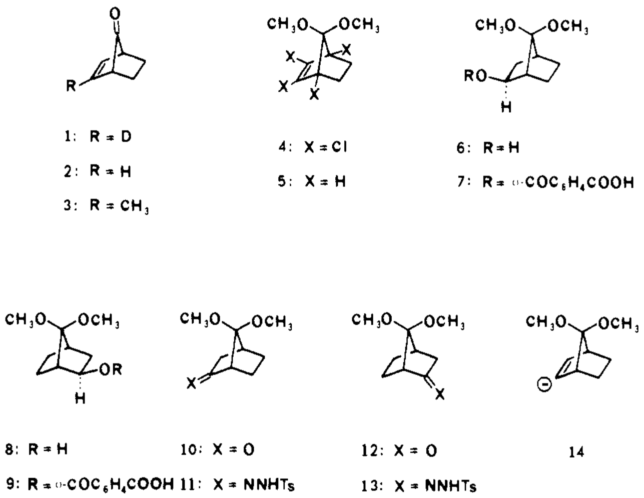
exhibits an n → π* transition (ϵ_{275} 33, isooctane)[3] that is hypsochromically shifted but shows no enhanced absorption relative to the saturated ketone analogue, 7-norbornanone (ϵ_{287} 32, isooctane).[3] Hückel calculations on the two ketones predicted a hypsochromically shifted n → π* transition and a bathochromically shifted π → π* transition for **2** relative to 7-norbornanone, with the conclusion that the UV data are "fully consistent with the delocalized system".[7] Failure of **2** to show an intensified n → π* absorption was ascribed to a "lack of overlap".[6] Subsequently, other workers prepared samples of **2** that showed no detectable maximum near 233 nm.[8-10] Similarly, a sample of 1,5,5-trimethylbicyclo[2.2.1]hept-2-en-7-one was reported to show a hypsochromically shifted n → π* transition (ϵ_{270} 58, ethanol), but "at lower wavelengths it shows only ill-defined absorption rising to ε 3000 at ca. 200 mμ".[11] It was therefore concluded that Norton's 233-nm absorption band[3] was in error and there was no evidence for interaction of the two π systems and therefore no charge-transfer absorption.[12]

During the period of controversy, Orloski[10,13] prepared a very carefully purified sample of **2**, examined its UV spectrum in a variety of solvents, and concluded from his own studies that Norton's 233-nm band was erroneous—but only to the extent that it was not in the position reported by Norton and did not have the reported intensity. Orloski also called the band a charge-transfer band and noted that it was difficult to locate. The band appeared as a broad shoulder near 215 nm in *n*-heptane and near 220 nm in 95% ethanol. It showed a "red shift" as solvent polarity increased and appeared as a broad absorption with a maximum at 223 nm (ε 583) in 2,2,3,3-tetrafluoropropanol. Orloski[13] attributed it to a $\pi_2 \rightarrow \pi_3$ excitation, in the language of Labhart and Wagnière.[14] More recently, ^{13}C NMR evidence has been invoked as evidence for interaction of the π systems in **2**: the chemical shifts of the carbonyl carbons are δ 205.1 for **2** and 216.2 for 7-norbornanone.[15]

Interaction of Chromophores. The effects and nature of the electronic interaction of C=O and C=C chromophores in β,γ-unsaturated ketones have been the subject of wide and varied investigations for many years.[2a,4-11,13-16] Those homoconjugated ketones that exhibit enhanced intensity and a bathochromic shift of the long-wavelength n → π* transition, e.g., 2-norbornenone, were of special interest and have been examined in detail, both experimentally[16,17] and theoretically.[14,16,18-20] Enhanced absorption and wavelength shifts or new bands were attributed earlier to intramolecular "charge transfer".[5,14,21] However, the importance of charge transfer must be evaluated on a case-by-case basis because it has been shown that wavelength-shifted electronic transitions and new transitions may be explained better by electrostatic coupling of locally excited states from the C=O and C=O chromophores.[18-20] For example, Hansen[19] has shown that the enhanced 296-nm transition and associated rotatory properties of chiral bicyclo[2.2.2]oct-5-en-2-one are explained by mixing of the locally excited C=O n → π* state with the C=C π → π* state. The transition involves essentially no charge-transfer components, and the charge-transfer contributions to the 197-nm transition are also small.

Chart I


1: R = D
2: R = H
3: R = CH$_3$
4: X = Cl
5: X = H
6: R = H
7: R = o-COC$_6$H$_4$COOH
8: R = H
9: R = o-COC$_6$H$_4$COOH
10: X = O
11: X = NNHTs
12: X = O
13: X = NNHTs
14

It is clear that attempts to extract the characteristics of weak electronic absorption bands from a manifold of broad, overlapping UV bands may well be frustrating and inconclusive. Circular dichroism (CD) spectra, on the other hand, tend to be better resolved than UV spectra due to the signed nature of the bands, and the rotatory intensities provide an additional aid to making assignments of the transitions. The electronic transitions of even symmetric chromophores may be made chiral by an appropriate chirally situated perturbing group, and if the perturbation is sufficiently small, the electronic nature of the excitations remains essentially unaffected.

Chiral β,γ-unsaturated ketones may not show the effects of perturbers when the double bonds are dissymmetrically oriented, because the rotatory contribution of the extended (inherently dissymmetric[22,23]) chromophore may overwhelm the extrachromophoric contributions and control the sign and magnitude of the Cotton effect (CE). However, the domination vanishes when the double bonds are coplanar, orthogonal, or otherwise symmetrically disposed. Here the rotatory strength and CD sign are controlled by the extrachromophoric static dissymmetric perturbers.[24,25] As we shall show, both a deuterium atom and a methyl group serve effectively as dissymmetric perturbers of the electronic transitions of the symmetric homoconjugated ketone, 7-norbornenone.

In our circular dichroism (CD) studies of isotopic perturbation of symmetric chromophores in rigid systems,[26] the preparation and chiroptical analysis of 2-deuterio-7-norbornenone (**1**) offered a new way to examine both the effect of chiral deuterium perturbers and the controversial charge-transfer band of 7-norbornenone (**2**) (Chart I). In what follows, we shall describe the syntheses of **1**, **2**, and 2-methyl-7-norbornenone (**3**) of known

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(12) Relevant comments include "β,γ-unsaturated ketones of this structural type show *neither* charge transfer *nor* enhanced n–π* absorption";[11] "from a spectroscopic point of view there is little, if any, nonconjugated interaction of the two π-systems";[8b] "we have no explanation for the short wave-length absorption observed by Norton".[9] It was believed by R. B. Woodward that Norton's data were spurious and due to the presence of a small amount of mesityl oxide (ref 13, p 62).

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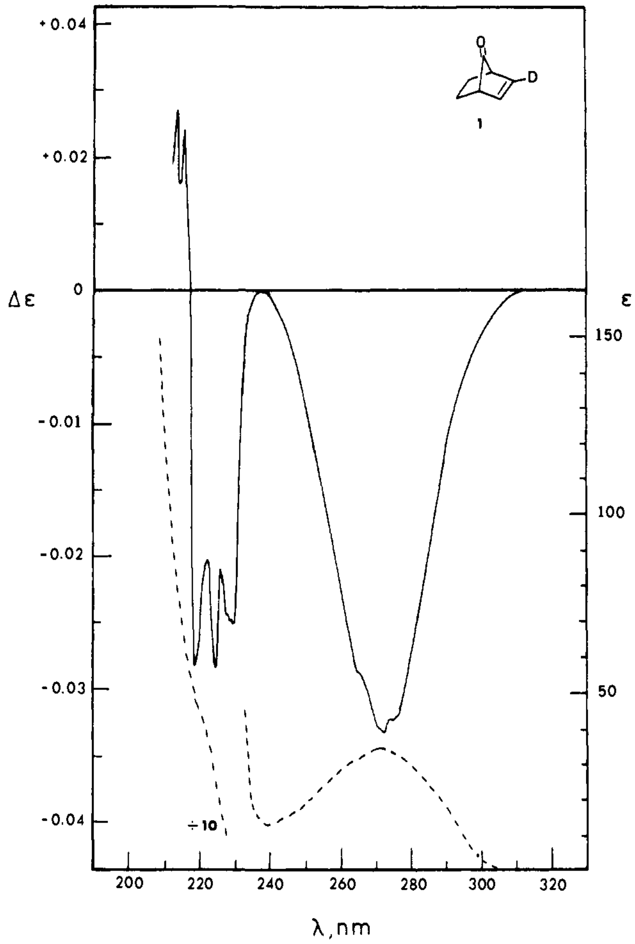

Figure 1. Circular dichroism (CD) (—) and ultraviolet (UV) (---) spectra of (1*R*)-2-deuteriobicyclo[2.2.1]hept-2-en-7-one (1) in *n*-heptane at 25 °C using 10^{-3} M solutions and 10- or 1-mm path lengths. The CD spectrum of the d_0 analogue (7-norbornenone, 2) serves as the CD baseline (Δε 0) for 1.

enantiomeric excess (ee) and absolute configuration and their UV and CD spectra. We then follow with a discussion of the low-lying transitions in the light of preliminary calculations.

Synthesis and Absolute Configuration

The important chiral intermediate **6** was made available by procedures developed in our earlier work.[27,28] Thus, racemic hydroxy ketal (**6** + **8**)[29] was prepared by oxymercuration of the well-known ketal **5**, which is available from the Diels–Alder reaction product (**4**) of 1,1-dimethoxy-2,3,4,5-tetrachlorocyclopentadiene with ethylene.[30] An improved dechlorination step using sodium/liquid NH_3[28] allows for the smooth conversion of **4** to **5** in high yield. Crystallization of the racemic half-acid phthalate (**7** + **9**) *l*-ephedrine salt in dioxane gave resolved material suitable for conversion to **1** and **3**. Upon hydrolysis, the less crystalline diastereomer gave (+)-alcohol that proved to be mainly enantiomer **6**, as determined by its chemical conversion to (1*S*)-norcamphor[27] or ^{19}F LIS-NMR spectra of its Mosher ester.[28,31] The enantiomeric excess of **6** was determined by NMR spectroscopy using its Mosher ester[31] or directly on the alcohol (**6**) using tris[3-[(trifluoromethyl)hydroxymethylene]-*d*-camphorato]europium(III) to separate the diastereotopic syn OCH_3 groups.[27,28]

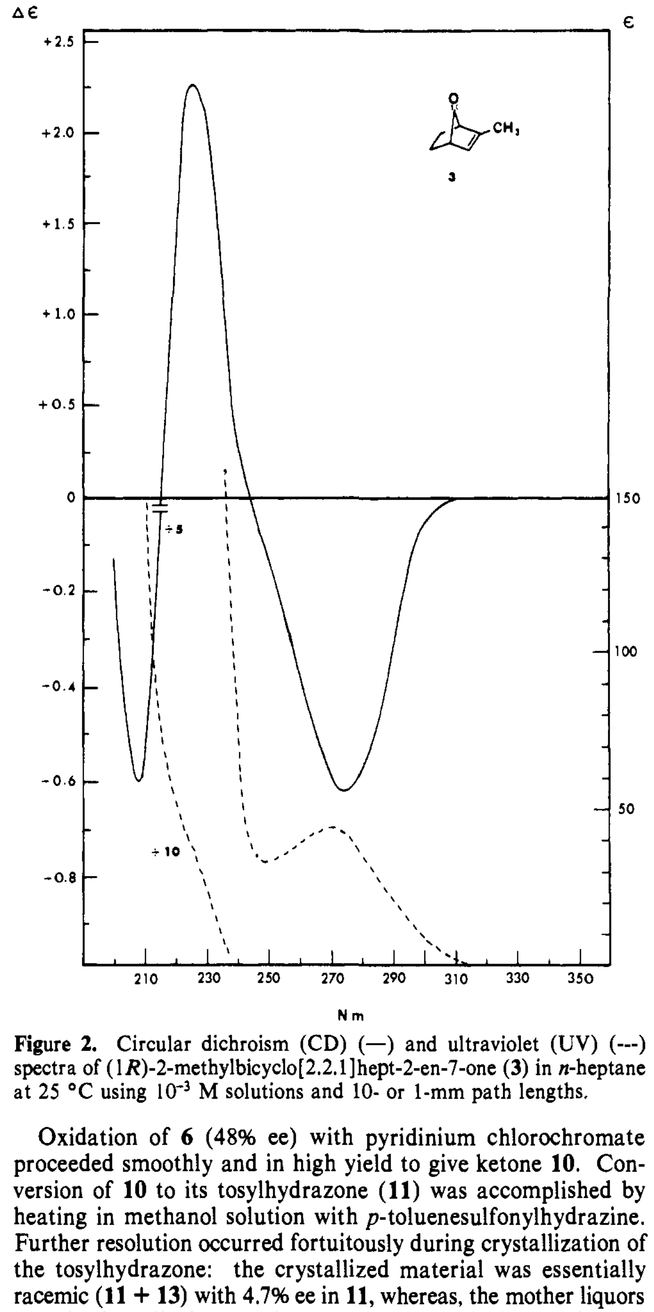

Figure 2. Circular dichroism (CD) (—) and ultraviolet (UV) (---) spectra of (1*R*)-2-methylbicyclo[2.2.1]hept-2-en-7-one (3) in *n*-heptane at 25 °C using 10^{-3} M solutions and 10- or 1-mm path lengths.

Oxidation of **6** (48% ee) with pyridinium chlorochromate proceeded smoothly and in high yield to give ketone **10**. Conversion of **10** to its tosylhydrazone (**11**) was accomplished by heating in methanol solution with *p*-toluenesulfonylhydrazine. Further resolution occurred fortuitously during crystallization of the tosylhydrazone: the crystallized material was essentially racemic (**11** + **13**) with 4.7% ee in **11**, whereas, the mother liquors contained tosylhydrazone that was 95% ee in **11**. (The ee in each instance was determined by conversion back to starting ketone with *N*-bromosuccinimide.[32]) Because this was the only crystallization step in the reaction sequence following the primary resolution, the ee of **1** and **3** could be known from the ee of their precursor tosylhydrazone. A modified Shapiro–Heath olefin synthesis[33] using CH_3Li in TMEDA[26] gave the ketal of **1** with D_2O quenching of the intermediate vinyl anion (**14**) and the ketal of **3** with CH_3I quenching.[34] The use of TMEDA as solvent minimized CH_3Li addition to the C=N bond[26] of **11** and also allowed us to obtain **1** with 97–100% d_1 incorporation.[35] Dekctalization in glacial acetic acid gave **1** and **3**.

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[34] Quenching the dark red intermediate vinyl carbanion (**14**) of the Shapiro–Heath reaction at room temperature with CH_3I led to a complex mixture of products. One of the isolated products, after deketalization, was 2,3-dimethylbicyclo[2.2.1]hept-2-en-7-one.

[35] The Shapiro–Heath reaction in this crowded system was slow (24 h at room temperature) and moderate in yield. Use of *n*-butyllithium gave a complex mixture of products. Quenching the intermediate carbanion (**14**) required low temperature in order to prevent overheating due to the exothermic nature of the reaction. For example, quenching with D_2O at room temperature gave the ketal of **1** with only 85–89% d_1 incorporation.

Circular Dichroism Spectra

The CD and UV curves for **1** and **3** are shown in Figures 1 and 2. Comparison of the ordinary and rotatory properties clearly shows that CD spectroscopy is much more reliable than UV spectroscopy in detecting weak or otherwise hidden electronic transitions. Thus, the existence of a weak, short wavelength transition (near 225 nm) in 7-norbornenone is fully manifest, a transition corresponding apparently to the widely discussed but elusive charge-transfer band that appears at best only as a shoulder or inflection in the UV spectrum. A compilation of UV spectral data for **1**–**3** and structurally related β,γ-unsaturated ketones or chromophoric components, all from a variety of sources, is presented in Table I. Again, the difficulty or uncertainty in locating the weak UV transition near 225 nm in the symmetric homoconjugated ketones is evident.

The UV spectral data for **3** (Figure 2 and Table I) are interesting in that they show no intensity enhancement or wavelength shift (relative to **1** or **2**) for the long-wavelength transition. As with **1** and **2**, the shorter wavelength transitions are even more difficult to discern. The CD spectrum, however, clearly shows transitions at 275 and 226 nm, both the 10- to 100-fold increases in $\Delta\epsilon$ values over the corresponding transitions of **1**. The transition at 208 nm of **3** appears to be a new one with a recognizable counterpart in the CD spectrum of **1**.

Curiously, **1** and **3** have the same CE signs for the 270–275-nm transitions, whereas comparison of deuterium and methyl perturbers in most saturated alkyl ketones studied[36] show that the n → π^* transitions are oppositely signed for the same absolute stereochemistry.[28,36] The CD behavior of **1** and **3** is akin to that of the corresponding *exo*-2-deuterio- and *exo*-2-methylbicyclo[2.2.1]heptan-7-ones[27,28] (**15** and **16**, Table II) where the dissymmetric perturbers are close to the third nodal surface.[37] Insofar as the octant rule[37,38] might be applied to the long-wavelength electronic transition of **3** (shown in our calculations to be mainly a C=O n → π^* type), it might be argued that the methyl perturbers of both **3** and its saturated *exo*-analogue **16** lie in front octants (explaining the negative CEs), whereas the deuterium perturbers of **1** and **15** lie in back octants and thus give the expected dissignate contribution.[28] These data may be compared with those for the relevant *endo*-2-deuterio- and *endo*-2-methylbicyclo[2.2.1]heptan-7-ones (**17** and **18**, Table II), both of whose dissymmetric perturbers lie in back octants and give the expected octant contributions.

Discussion

The computed signs and magnitudes of carbonyl CD CE's depend crucially upon rather small contributions to the total wave functions.[39d] Moreover, the position of the deuterium atom or methyl group on the 7-norbornenone skeleton is close to a sign-determining surface[28,37] so that molecules **1** and **3** can be expected to be particularly demanding with respect to details of the wave functions.

We attempted to characterize the lowest-lying electronic transitions in **1** and **3** by means of minimal-basis (STO-4G) SCF calculations[40] followed by the localized orbital random phase approximation (LORPA) for the excitation properties.[39] Computations were done on force-field optimized geometries[41,42] for the two systems. Our expectations concerning the sensitivity of the results for perturbers located at the 2 position were borne out, in that the calculations predicted the correct sign of the long-wavelength CE for **1**, but not for **3**. However, the calculations for both systems yielded three low-lying bands: the lowest one essentially an isolated carbonyl n → π^* excitation and two bands very close together in energy. The more intense (UV) of these can be identified almost completely with the olefinic $\pi \rightarrow \pi^*$ excitation. The other is predicted to be a mixed transition with a substantial (~15%) charge-transfer component of the form $\pi_{C=C} \rightarrow \pi^*_{C=O}$ but also with other major components originating in three different carbonyl in-plane $\sigma \rightarrow \pi^*$ excitations: ~15% $\sigma_{C-C_\alpha} \rightarrow \pi^*_{C=O}$, ~30% $n(\sigma)_{C=O} \rightarrow \pi^*_{C=O}$ and ~30% $\sigma_{C=O} \rightarrow \pi^*_{C=O}$.[43] This band corresponds to the disputed, weak 225-nm transition, previously called a charge-transfer band[4–6,13] and now clearly observed in the CD spectra of norbornenones **1** and **3**. It should be recognized, however, that although called a charge-transfer band, the transition is composed largely of in-plane carbonyl $\sigma \rightarrow \pi^*$ excitations mixed with a nontrivial (ca. 15%) and apparently significant charge-transfer component.

In summary, the existence of a weak electronic transition near 225 nm in 7-norbornenone is shown experimentally by CD measurements. And in agreement, molecular orbital calculations predict the existence of such a low-lying band and reveal that it contains inter alia a charge-transfer component. A more detailed theoretical study of the chiroptical properties of these systems is under way and will be reported separately.

Experimental Section

General Data. Circular dichroism spectra were recorded on a JASCO J-40 instrument equipped with a photoelastic modulator and CAT, ultraviolet spectra were recorded on a Cary 219 spectrophotometer, and sodium D-line rotations were determined in CH_2Cl_2, unless otherwise noted, on a Perkin-Elmer 141 polarimeter. All nuclear magnetic resonance spectra (60 MHz) were determined in CD_2Cl_2, unless otherwise indicated, on a Perkin-Elmer R-24B instrument and reported in ppm downfield from tetramethylsilane. Mass spectra were recorded at 70 eV on a JEOL JMS-07 spectrometer, and infrared spectra were recorded on a Perkin-Elmer model 599 spectrophotometer. All melting points are uncorrected and were determined on a Thomas Hoover apparatus. Preparative gas chromatography (GC) was performed on a Varian-Aerograph model 1700 instrument on column A (6 ft × $^3/_8$ in., 12% QF-1 on Chromosorb W) or column B (5 ft × $^1/_4$ in., 20% TCEP on Chromosorb P). Analytical GC was performed on a Varian-Aerograph model 2400 instrument on column C (6 ft × $^1/_8$ in., 5% FFAP on Chromosorb W). Combustion analyses were performed by Chemalytics, Tempe, AZ. Spectral data were obtained by using spectral grade solvents (MCB). Other solvents were distilled and dried prior to use: diethyl ether and tetrahydrofuran (from $LiAlH_4$) and dichloromethane (from P_2O_5) were used as freshly distilled or stored over 4A molecular sieves (Linde). Tetramethylethylenediamine (TMEDA), Aldrich, was distilled twice from CaH_2 and stored over 5A molecular sieves. Pyridine was distilled from BaO and stored over KOH. Column chromatography was accomplished on Florisil (Floridin Co.) or Merck neutral alumina. The deu-

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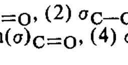
(41) Allinger, N. L. Program QCPE 318, Quantum Chemistry Program Exchange, Indiana University, Bloomington, IN.

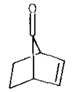
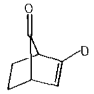
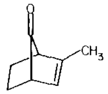
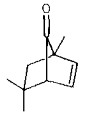
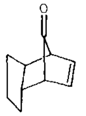
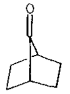
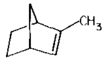
(42) Using the method of ref 41, the calculated optimized geometry for 7-norbornenone (structure **2** in Table II) is $\theta = 98.5$, $\psi = 114.3$, $\phi = 123.8°$. There is no experimentally determined geometry for **2**; however, there is for norbornene (structure **19**, Table II): $\theta = 95.3$, $\psi = 110.8 \pm 1.5$, $\phi = 122.3°$ were determined from a microwave study by: Chiang, J. F.; Chiang, R.; Lu, K. C.; Sung, E-M.; Harmony, M. D. *J. Mol. Struct.* **1977**, *41*, 67–77. Our calculated angles for norbornene ($\theta = 92.5$, $\psi = 112.2$, $\phi = 124.7°$) are in reasonably good agreement and lend credence to our contention that the optimized geometry calculated for 7-norbornenone is acceptable. Note that, as expected, the internal angle at C-7 is larger ($\theta = 98.5°$) in 7-norbornenone than in norbornene ($\theta = 95.5°$), reflecting the change in hybridization at C-7. And, interestingly, the experimentally derived interplanar angle ($\phi = 122.3°$) reveals that there is little, if any, tilt of C-7 toward the C=C in norbornene. A similar result appears in the optimized geometries of norbornene and 7-norbornenone.

(43) Component transitions associated with the carbonyl group (C=O) may be related to the following in-plane orbital diagram.



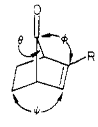
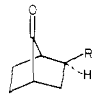
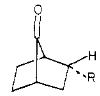
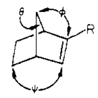
(1) $n_{C=O}$, (2) σ_{C-C_α},
(3) $n(\sigma)_{C=O}$, (4) $\sigma_{C=O}$

Table I. Ultraviolet Spectral Data for Bicyclic Ketones and Olefins Related to 7-Norbornenone

compd	solvent	ref	absorption λ_{max}, nm (ϵ)					
	isooctane	*a*	275 (31)	233 (1200)				
		b	275 (33)					
		c	274 (31)					
	n-heptane	*d*	273 (32)	215^{sh} (630)	203^{sh} (2680)	194.5^{sh} (4440)	189^{sh} (6340)	186^{sh} (6720)
		e	271 (35)	222^{infl} (370)				
	chloroform	*c*	273 (41)					
	ethanol	*c*	273 (43)					
		d	271 (39)	220^{sh} (490)				
		f	274 (36)	215 (500)				
		g	274 (31)					
		h	272 (38.9)	222^{infl} (465)				
		i, b		233 (1300)				
		j		233 (1290)				
		k		233 (250)				
	2,2,3,3-tetra-fluoropropanol	*d*	266 (49)	233 (58)	200^{sh} (2300)	185 (5080) not max		
	*n*-heptane	*e*	272 (35)	220^{infl} (450)	200 (3100) not max			
	*n*-heptane	*e*	273 (42)	227^{infl} (350)	200 (5000) not max			
	*n*-heptane	*d*	273 (42)	215^{sh} (1000)	206^{sh} (2850)	198^{sh} (4850)	188 (7140)	
	ethanol	*d*	268.5 (47)	220^{sh} (680)	206^{sh} (2240)	190 (6240)		
		l	270 (58)					
	isooctane	*m*	269 (30.6)	215^{sh} (800)	203^{sh}[o] (2900)			
		n, o	268 (33)	215^{sh} (800)	203^{sh}[o] (2900)	195.5^{sh}[o] (4400)	190^{sh}[o] (5300)	187.5 (6200)
	isooctane	*c*	293 (18)					
	chloroform	*c*	292 (12)					
		p	292 (18)					
	ethanol	*j*	287 (32)					
		r	290[q] (14)	215 (33) not max				
	*n*-heptane	*d*				196 (5310)		
	ethanol	*d*				196 (5310)		
	*n*-heptane	*e*				201 (7350)		

[a] Norton,[3] quoted in ref 6. [b] Norton,[3] quoted in ref 9. [c] Reference 8b. [d] Reference 13. [e] This work. [f] Reference 7, quoted by Pincock, R. E.; Haywood-Farmer, J. *Tetrahedron Lett.* **1967**, 4759–4762. [g] Reference 9, quoted in ref 13. [h] Reference 9. [i] Norton,[3] quoted in ref 8b. [j] Norton (ref 3), quoted in ref 13. [k] Reference 9, not a max or infl. [l] Reference 11. [m] Scherer, K. V., Abstracts, 144th National Meeting of the American Chemical Society, Los Angeles, April 1963, p 61M, quoted in ref 9. [n] R. B. Woodward, quoted in ref 13. [o] K. V. Scherer,[n] quoted in ref 8b. [p] Reference 8a. [q] Reference 7. [r] Pincock and Haywood-Farmer of ref 11.

Table II. Circular Dichroism Cotton Effect Data for Bicyclic Ketones, Corrected to 100% Enantiomeric Excess

	R = D		R = CH_3	
structure[a]	λ_{max}, nm ($\Delta\epsilon$)	$[R]$[b]	λ_{max}, nm ($\Delta\epsilon$)	$[R]$[b]
	273 (−0.033)	−0.097	275 (−0.62)	−1.8
	228 (−0.025)			
	224 (−0.028)	−0.021	226 (+2.10)	+1.4
	219 (−0.028)			
1, R = H	216 (+0.024)			
2, R = D	213 (+0.029)	+0.020	208 (−3.0)	−0.63
3, R = CH_3				
	296 (−0.033)	−0.078[c]	295 (−0.15)	−0.62[d]
15, R = D				
16, R = CH_3				
	292 (−0.132)	−0.37[c]	295 (+0.60)	+2.1[d]
17, R = D				
18, R = CH_3				
			212 (−7.3)	−2.1
19, R = H				
20, R = CH_3				

[a] Values for the various internal (θ) and interplanar (ψ and ϕ) angles are given in ref 42. [b] $[R]$ is the reduced rotatory strength, $[R] \approx R_K \times 1.08 \times 10^{40}$. [c] Data from: Lightner, D. A.; Gawroński, J. K.; Bouman, T. D. *J. Am. Chem. Soc.* 1980, *102*, 1983–1990. [d] Data from ref 27.

terium oxide used in this work was 99.8%, from Bio-Rad.

(1*R*)-7,7-Dimethoxybicyclo[2.2.1]heptan-2-one *p*-Toluenesulfonylhydrazone (11).[28] (−)-Ketone **10** (851 mg, 5 mmol, $[\alpha]_D^{25}$ −28.4°, 48% ee) was heated briefly to boiling with 931 mg (5 mmol) of *p*-toluenesulfonylhydrazine (Aldrich) in 5 mL of CH_3OH and allowed to stand at room temperature for 24 h. Part of the tosylhydrazone crystallized, was removed by filtration, and washed with ether–pentane to give 882 mg (52%) of product A with mp 188–190 °C dec and $[\alpha]^{25}_D$ +2.0° (*c* 1.2, $CHCl_3$). The mother liquor was evaporated to dryness to give a semisolid product (B), 810 mg (48%) with $[\alpha]^{25}_D$ +22.0° (*c* 1.4, $CHCl_3$) and mp 125–128 °C dec.

In order to ascertain the ee of A and B, each was converted separately back to its corresponding 7,7-dimethoxybicyclo[2.2.1]heptan-2-one by use of *N*-bromosuccinimide, as described previously.[28,32] The ketone regenerated from A had $[\alpha]^{25}_D$ −2.78° (4.7% ee) and that from B had $[\alpha]^{25}_D$ −56.1° (95% ee).

Racemic tosylhydrazone (**11** + **13**) was prepared from racemic ketone (170 mg, 1 mmol) and 186 mg (1 mmol) of *p*-toluenesulfonylhydrazine in 1 mL of CH_3OH. After 24 h at room temperature, the reaction mixture was evaporated to dryness under reduced pressure and washed with pentane to give a crystalline product, 338 mg (100%), mp 190–191 °C dec. (Tosylhydrazone of 48% ee had mp 175–182 °C dec.)

The tosylhydrazone had IR (Nujol): ν 3200, 2840, 1670, 1595, 1325, 1160 cm^{-1} and NMR ($CDCl_3$): δ 2.38 (s, 3 H, Ar-CH_3), 3.00 (s, 3 H, OCH_3), 3.16 (s, 3 H, OCH_3), 7.20 (d, *J* = 8 Hz, 2 H, Ar), 7.74 (d, *J* = 8 Hz, 2 H, Ar). Anal. Calcd for $C_{16}H_{22}O_4N_2S$ (338.43): C, 56.78; H, 6.55; N, 8.28. Found: C, 57.01; H, 6.41; N, 8.16.

(1*R*)-2-Deuteriobicyclo[2.2.1]hept-2-en-7-one (1). Tosylhydrazone **11** (329 mg of 48% ee mixed with 398 mg of 95% ee gave 727 mg, 2.15 mmol, average ee = 74%) was suspended in dry TMEDA (4 mL) and treated under N_2 at −50 °C with 6 mL of 1.6 M CH_3Li (4.4 equiv). The mixture was allowed to warm to room temperature to produce a dark brown solution (total reaction time = 21 h). After recooling to −30 °C, 0.30 mL of 99.8% D_2O was added, and the slightly yellow resultant mixture was allowed to warm to room temperature. It was extracted with pentane–water, and the organic phase was washed with 2 N aqueous HCl followed by 3 N aqueous NaOH. The dried ($MgSO_4$), colorless extract was concentrated by solvent distillation through a vigreaux column. It was then deketalized by stirring under N_2 with 2.5 mL of glacial acetic acid and 0.1 mL of concentrated HCl for 6 h. The deketalization was complete in 3 h according to GC on column B. The reaction was worked up with 16 mL of 3 N aqueous NaOH and pentane to give 55 mL of colorless extract, which was purified by preparative GC on column A, to yield 55 mg (51%) of a colorless liquid. An analytical sample of >99.9% purity according to analytical GC on column C was obtained by repeated preparative GC. The NMR showed the sample to be 97% d_1 and 3% d_0; MS showed it to be 100% d_1. It had CD (*n*-heptane): Δ_{273}^{max} −0.033, $\Delta\epsilon_{224}^{max}$ −0.028, $\Delta\epsilon_{213}^{max}$ +0.029 (corrected to 100% ee); UV (*n*-heptane): ϵ_{272}^{max} 35, ϵ_{220}^{infl} 450, ϵ_{200} = 3100; NMR: δ 1.0–2.2 (m, 4 H), 2.78 (br s, 2 H), 6.48 (t, *J* = 2 Hz, 1 H); MS, *m*/*z* (relative intensity) 81 (M − CO) (86%), 80 (100%) amu.

Bicyclo[2.2.1]hept-2-en-7-one (7-Norbornenone, 2).[8,9,13] A solution of the ketal (**5**) (490 mg, 3.18 mmol) in glacial acetic acid (3 mL) was heated under N_2 for 10 h (oil bath at 110 °C). The resulting solution was cooled, extracted with pentane and 20 mL of 3 N aqueous NaOH, and the extract was washed with saturated aqueous NaCl. The dried ($MgSO_4$) extract was concentrated by column distillation and the product separated by preparative GC on column A to give a colorless oil (236 mg) in 68% yield. An analytical sample of >99.9% purity (GC on column C) was obtained by repeated preparative GC. It had UV (*n*-heptane): ϵ_{271}^{max} 35, ϵ_{222}^{infl} 370; NMR: δ 1.0–2.3 (m, 4 H), 2.80 (m, 2 H), 6.43 (t, *J* = 2.5 Hz, 2 H); MS, *m*/*z* (relative intensity) 80 (M − CO) (100%), 79 (100%) amu.

(1*R*)-2-Methylbicyclo[2.2.1]hept-2-en-7-one (3). A suspension of tosylhydrazone **11** [1.69 mg, 5.0 mmol, $[\alpha]^{25}_D$ −17.7° ($CHCl_3$), 30% ee] in 10 mL of dry TMEDA was treated under N_2 at −65 °C with 14 mL of 1.6 M CH_3Li (4.5 equiv). The dark brown mixture was allowed to warm slowly to room temperature (total reaction time = 22 h). After recooling to −60 °C, the reaction was quenched with 2.0 mL (31 mmol) of CH_3I (filtered through Activity III neutral Al_2O_3) dissolved in 10 mL of dry pentane. The CH_3I solution was precooled to −70 °C and added at once with efficient stirring. The sticky, almost colorless reaction mixture was allowed to warm slowly to room temp (2.5 h) and worked up with pentane and water. The organic phase was washed with 2 M aqueous HCl and then 3 N aqueous NaOH and dried ($MgSO_4$). The pentane and ether were removed by careful distillation through a vigreaux column. GC (column C) showed the presence of two ketals as the main products.

The crude, concentrated product was heated at 110 °C (oil bath temp) under N_2 with 4 mL of glacial acetic acid for 1.5 h. GC (column C) showed complete hydrolysis of the ketals. The solution was cooled and then pentane–ether and 26 mL of 3 N aqueous NaOH were added. The organic layer was separated and filtered through Activity II silica gel to give a colorless solution of the ketones. The solution was concentrated by careful distillation of the solvents through a vigreaux column. The ketones (a 2:1 mixture of **3** and **2**) were separated and purified by preparative GC (column A). Ketone **3** was carefully purified further on column B to give a sample of >99.9% purity. It had CD (*n*-heptane): $\Delta\epsilon_{275}^{max}$ −0.62, $\Delta\epsilon_{226}^{max}$ +2.10, $\Delta\epsilon_{208}^{max}$ −3.0 (corrected to 100% ee); UV (*n*-heptane): ϵ_{270}^{max} 43, ϵ_{200} 5000 (not λ_{max}); NMR:[44,45] δ 1.0–2.2 (m, 4 H), 1.86 (d, *J* = 1.8 Hz, 3 H, CH_3), 2.58 (m, 1 H), 2.78 (m, 1 H), 6.05 (m, 1 H); MS, *m*/*z* (relative intensity) 94 (M − CO) (72%), 79 [M − CO − CH_3] (100%) amu.

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(44) Moss, R. A.; Ho, C.-T. *Tetrahedron Lett.* **1976**, 3397–3400.

(45) Cargill, R. L.; Sears, A. B.; Boehm, J.; Willcott, M. R. *J. Am. Chem. Soc.* **1973**, *95*, 4346–4355.