Table I. ¹H Nmr parameters (τ Values) of 6, 7, 11, and 12 at 60 MHz (Internal Standard, TMS)

Compd	Hα	Hβ	Hγ	Allylic CH₂	Nonallylic CH₂	CH₃
6 (CDCl₃)	3.82 (d)a	0.94 (d)a		7.7 (m)	8.3 (m)	
6 (CF₃COOD)	3.63 (d)a	0.07 (d)a		7.7 (m)	8.2 (m)	
7 (CDCl₃)b	3.84 (d)a	1.06 (d)a		7.7 (m)	8.3 (m)	
7 (CF₃COOD)	3.57 (d)a	0.13 (d)a		7.6 (m)	8.2 (m)	
11 (CDCl₃)	3.87 (d)a	1.17 (d of d)c	3.47 (d)d			7.97 (s)
11 (CF₂COOD)	3.70 (d)a	0.30 (d of d)c	3.43 (d)d			7.99 (s)
12 (CF₃COOD)e	3.67 (d)a	0.37 (d of d)c	3.30 (d)d			7.93 (s)

a $J = 16$ Hz. b The spectrum of 7 in CDCl₃ was determined on a Bruker HFX-90 instrument (90 MHz, fast Fourier transform, 2000 scans), due to its low solubility in this solvent. c $J = 16, 12$ Hz. d $J = 12$ Hz. e The spectrum of 12 in CDCl₃ was not determined, due to its low solubility in this solvent.

crystals,[7,10] eluted before 4). Substance 4 was identical with that obtained by an unambiguous route,[2] and could be further coupled under "Glaser conditions" (2 hr at 65°) to give the previously described[2] bright red 1,6-dione 6[11] in 50% yield. On the other hand, the isomeric diketone 5 could not be coupled under "Glaser conditions" and decomposed under "Eglinton conditions" (cupric acetate in pyridine).[9] However, coupling of 5 with oxygen, cuprous chloride, and N,N,N',N'-tetramethylenediamine in acetone ("Hay conditions")[12] for 2 hr at 30°, followed by repeated filtration through silicic acid, gave 30% of the 1,10-dione 7 as sparingly soluble bright yellow needles:[10] m/e 364; λmax (CHCl₃) 272 sh (ϵ 21,400), 287 (28,800), 304 (30,800), 329 sh (24,700), 346 (27,900), 367 nm (27,600), with absorption at >500 nm; νmax (KBr) 2210 (m), 2140 (w) (C≡C), 1620 (s) (C=O) cm⁻¹.

The starting material for the synthesis of the diketones 11 and 12 was cis-3-methyl-2-penten-4-ynal,[13] which was homologated to the liquid aldehyde 8[7,14] in 70% yield by the method used for the synthesis of 1. Substance 8 was then converted to the ketone 10 (mp 76–77.5°)[7] via the alcohol 9 in 55% overall yield, as described for the transformation of 1 to 3. Finally, coupling of 10 under "Glaser conditions" for 2 hr at 60° directly led to the diketones 11 and 12.

The relatively soluble diketone 11 was removed from the reaction residue by trituration with chloroform. Chromatography on silica gel yielded 13% of 11 as orange needles:[10] m/e 284; λmax (CHCl₃) 279 sh (ϵ 27,100), 298 sh (27,600), 316 (53,500), 328 (48,400), 448 nm (3800), with absorption at >550 nm; νmax (Nujol) 2220 (w), 2160 (m) (C≡C), 1625 (s) (C=O) cm⁻¹. The very insoluble diketone 12 remaining in the reaction residue was taken up in a large volume of chloroform. Purification by repeated filtration through silicic acid gave 5% of 12 as yellow needles:[10] m/e 284; λmax (CHCl₃) 269 sh (ϵ 22,800), 284 (34,700), 300 (44,900), 333 sh (36,900), 343 (38,000), 361 nm (32,900), with absorption at >500 nm; νmax (Nujol) 2220 (m), 2160 (w) (C≡C), 1625 (s) (C=O) cm⁻¹.

The tetradehydro[18]annulenediones 6, 7, 11, and 12 dissolved in CF₃COOH to form highly colored solutions: longest wavelength λmax 6, 510 nm; 7,

(10) The substance decomposed on attempted melting point determination.
(11) For comparison with 7, 11, and 12, the electronic spectrum of 6 was determined in chloroform: λmax 277 (ϵ 16,800), 296 (22,900), 315 (31,200), 336 (30,200), 464 nm (3000), with absorption >550 nm.
(12) See A. S. Hay, J. Org. Chem., 27, 3320 (1962).
(13) E. R. H. Jones and B. C. L. Weedon, J. Chem. Soc., 937 (1946); I. M. Heilbron, E. R. H. Jones, and M. Julia, ibid., 1430 (1949).
(14) The synthesis of 8 was carried out by Dr. J. Ojima, and we thank him for providing a sample.
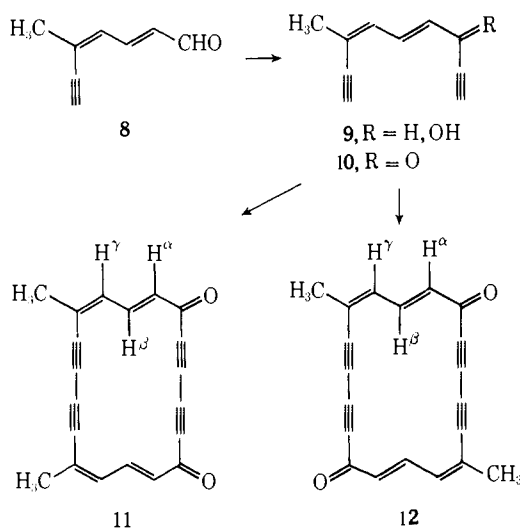
454 sh nm; 11, 488 nm; 12, 450 sh nm. The ¹H nmr spectra of 6, 7, 11, and 12 in CDCl₃ and CF₃COOD are given in Table I. They confirm the structures of these diketones and give no indication of any appreciable ring current. The relative structural assignments of 11 and 12 follow unequivocally from the correspondence of the electronic spectrum of 11 with that of 6[11] and of 12 with that of 7. The assignments of 11 and 12 are confirmed by their colors and relative solubilities, and the correspondence of the ir spectra in several respects with those of 6 and 7, respectively.

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Electrochemistry of Some Tetradehydro[18]annulenediones

Sir:

Recently several tetradehydro[18]annulenediones have been prepared.[1,2] These can be considered to be quinones related to the corresponding tetradehydro-[18]annulene[3] in the same way that benzoquinone is related to benzene. Since the reduction potentials

(1) K. Yamamoto and F. Sondheimer, Angew. Chem., 85, 41 (1973); Angew. Chem., Int. Ed. Engl., 12, 68 (1973).
(2) N. Darby, K. Yamamoto, and F. Sondheimer, J. Amer. Chem. Soc., 96, 248 (1974).
(3) T. Nomoto, K. Fukui, and M. Nakagawa, Tetrahedron Lett., 3253 (1972).

of various quinones reflect in part the aromatic stabilization of the related conjugated hydrocarbon system, it was of considerable interest to evaluate the electrochemical reduction potentials of these annulenediones as indications of the aromatic stabilization inherent in the related tetradehydro[18]annulene system. We now wish to report that these annulenediones can indeed be easily reduced to the corresponding dianions (e.g., $1 \rightarrow 2$).

1   2

3   4
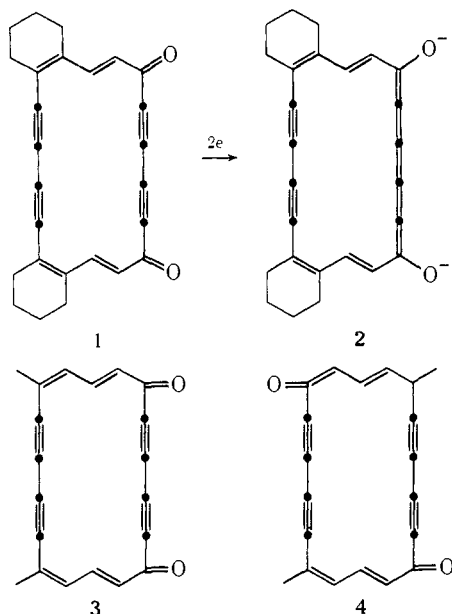
The electrochemical reduction of diones **1**, **3**, and **4** was examined by cyclic voltammetry along with a series of reference compounds. All measurements were performed at $20.0 \pm 0.3°$ in carefully dried purified[4] dimethylformamide with 1.0 M tetrabutylammonium perchlorate as supporting electrolyte. Substrates were present at 0.4–1.0 mM, and the reduction potentials were determined under an argon atmosphere in a standard three-electrode cell. The working electrode was a platinum disk, the platinum wire auxiliary electrode was isolated from the bulk solution by a medium-porosity frit, and the reference electrode was a silver|silver chloride wire in the solvent–electrolyte medium isolated by an asbestos fiber tip. Voltammograms were generated using a PAR 173 potentiostat, a PAR 175 universal programmer, and a Tectronix 5103N storage oscilloscope. The half-wave potentials were obtained by extrapolating the midpoint of the cathodic and anodic peaks to zero scan rate,[5] and these potentials are listed in Table I.

All the compounds listed showed chemical and electrochemical reversibility at both the first and second waves, although dibenzoyldiacetylene showed anodic reoxidation waves only at higher scan rates (1–10 V/sec). The first wave corresponds to addition of one electron to produce the anion radical of the substrate, while the second wave is addition of a second electron to produce the corresponding dianion.[6] The sum of these poten-

(4) L. R. Faulkner and A. J. Bard, *J. Amer. Chem. Soc.*, **90**, 6284 (1968).

(5) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964); D. S. Polcyn and I. Shain, *Anal. Chem.*, **38**, 370 (1966). We used scan rates of 0.2–2.0 V sec^{-1}, and observed peak–peak separations of 56 to 84 mV over this range.

(6) C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Nonaqueous Systems," Marcel Dekker, New York, N. Y., 1970, Chapter 6; R. H. Philp, Jr., R. L. Flurry, and R. A. Day, *J. Electrochem. Soc.*, **111**, 328 (1964).

Table I. Electrochemical Reduction Potentials[a]

Compound	E_1	E_2	$E_1 - E_2$	$E_1 + E_2$
p-Benzoquinone	−0.52	−1.40	0.88	−1.92
1,4-Naphthoquinone	−0.64	−1.47	0.83	−2.11
9,10-Anthraquinone	−0.93	−1.63	0.70	−2.56
trans-Dibenzoylethylene	−0.92	−1.58	0.66	−2.50
Dibenzoylacetylene	−0.92	−1.58	0.66	−2.50
Dibenzoyldiacetylene	−0.83	−1.33	0.50	−2.16
Dicyclohexenoannulenedione (**1**)	−0.70	−1.04	0.34	−1.74
Dimethylannulenedione (**3**)	−0.66	−0.94	0.28	−1.60
Dimethylannulenedione (**4**)	−0.68	−0.93	0.25	−1.61

[a] At $20.0 \pm 0.3°$ in dry dimethylformamide as described in the text. Potentials relative to Ag|AgCl reference electrode.

tials, $E_1 + E_2$, thus reflects the total energy change involved in the conversion of the dione to the dianion.

As expected from the above considerations, reduction of benzoquinone is easier than reduction of naphthoquinone, while anthraquinone is the most difficultly reduced of the three. These results directly parallel expectations based on the increase in aromatic stabilization of the quinone on conversion to the aromatic hydroquinone dianion system. On this basis, the results with the three annulenediones **1**, **3**, and **4** are truly striking: $(E_1 + E_2)$ for the three is more positive than the value for benzoquinone. We can also compare diones **1** and **3** with dibenzoyldiacetylene, a mode for the right-hand side of the molecule. From Table I, 0.4–0.5 eV greater ease of reduction is found for the fully conjugated systems.[7]

If the increased aromatic character of the resulting dianion were the only determining factor in these potentials, they would indicate that the annulene system is considerably (0.3 eV, 7 kcal/mol) more stabilized by cyclic π-electron delocalization than is benzene itself. However, these potentials are also influenced by electrostatic factors, and this is seen most clearly in Table I in the column reflecting the difference in reduction potentials for the first and second waves, $(E_1 - E_2)$. The difference in potential for the addition of these two electrons, which to the simplest approximation are entering the same orbital, is the result of electrostatic repulsion effects. As Table I shows, the energy gap is much larger for small molecules such as benzoquinone than it is for the large annulenedione systems. In fact, if we consider only the *first* reduction potential we see that the annulenediones are not as easily reduced as is benzoquinone, although they are still comparable to naphthoquinone. A decrease in $(E_1 - E_2)$ is also seen if we compare dibenzoyldiacetylene, with its two carbonyl groups further apart, with dibenzoylacetylene whose two carbonyl groups are closer. The finding of almost identical potentials for **3** and **4** is reasonable, since the carbonyl groups are too far apart for much electrostatic interaction in either case.

These considerations frustrate any simple attempt to translate $\Delta(E_1 + E_2)$ directly into "resonance energy," but they do not detract from the clear experi-

(7) A direct open analog of **1**, in which[1] the right-hand diethinyl system is uncoupled so the molecule has two –CO—C≡C—H termini, undergoes irreversible one-electron electrochemical reduction at much more negative potentials.

mental evidence that **1**, **3**, and **4** are very easily reduced at both E_1 and E_2. By this experimental criterion it is certainly reasonable to consider that these annulene-diones are indeed quinones of an aromatic system.

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Infrared Circular Dichroism of Carbon–Hydrogen and Carbon–Deuterium Stretching Modes. Observations

Sir:

We report here the first measurements of optical activity arising from vibrations of molecules in the liquid state. Circular dichroism (CD) associated with the C*–H stretch (2920 cm^{-1}) is detected in the optically active liquids (S)-(+)- and (R)-(−)-2,2,2-trifluoro-1-phenylethanol, $CF_3CHOHC_6H_5$ (I). CD is also found at the C*–D stretch (2204 cm^{-1}) of (R)-(−)-neopentyl-*1-d* chloride, $(CH_3)_3CCHDCl$ (II). In our accompanying communication[1] the vibrational rotational strengths of these normal modes are calculated.

In contrast to optical activity arising from electronic transitions, which is readily measured in the visible and uv, Cotton effects of molecular vibrations had long eluded detection.[2] However, recent calculations[3–5] indicated the anticipated size of the vibrational effect and the kinds of structural information, such as absolute configuration or molecular conformation, which are latent in its measurement. Improved instruments have recently permitted the measurement of vibrational optical activity first in liquid crystals,[6] then in single crystals,[7] and now in fluids; our instrument has been previously described[8] except that a multiscan signal averager has been added. Observations of Raman circular intensity differentials[9] complement the present study.

In Figure 1 are shown the absorption and CD spectra

(1) T. R. Faulkner, A. Moscowitz, G. Holzwarth, E. C. Hsu, and H. S. Mosher, *J. Amer. Chem. Soc.*, **96**, 252 (1974).
(2) (a) T. M. Lowry, "Optical Rotatory Power," Longmans Green and Co., London, 1935, Chapter 18; (b) H. R. Wyss and H. H. Günthard, *Helv. Chim. Acta*, **49**, 660 (1966).
(3) C. W. Deutsche and A. Moscowitz, *J. Chem. Phys.*, **49**, 3257 (1968); **53**, 2630 (1970).
(4) G. Holzwarth and I. Chabay, *J. Chem. Phys.*, **57**, 1632 (1972).
(5) J. A. Schellman, *J. Chem. Phys.*, **58**, 2882 (1973).
(6) (a) B. Schrader and E. H. Korte, *Angew. Chem.*, **84**, 218 (1972); (b) I. Chabay, *Chem. Phys. Lett.*, **17**, 283 (1972); (c) R. J. Dudley, S. F. Mason, and R. D. Peacock, *J. Chem. Soc., Chem. Commun.*, 1084 (1972); (d) G. Holzwarth, I. Chabay, and N. A. W. Holzwarth, *J. Chem. Phys.*, **58**, 4816 (1973).
(7) E. C. Hsu and G. Holzwarth, *J. Chem. Phys.*, in press.
(8) I. Chabay, E. C. Hsu, and G. Holzwarth, *Chem. Phys. Lett.*, **15**, 211 (1972).
(9) (a) B. Bosnich, M. Moskowitz, and G. A. Ozin, *J. Amer. Chem. Soc.*, **94**, 4750 (1972); (b) L. D. Barron, M. P. Bogaard, and A. D. Buckingham, *ibid.*, **95**, 605 (1973); *Nature (London)*, **241**, 113 (1973); (c) L. D. Barron and A. D. Buckingham, *J. Chem. Soc., Chem. Commun.*, 152 (1973); (d) M. Diem, J. L. Fry, and D. F. Burow, *J. Amer. Chem. Soc.*, **95**, 254 (1973).
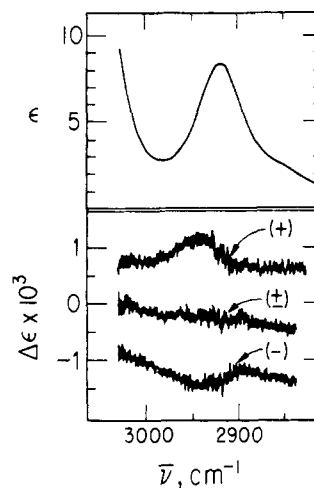
Figure 1. Infrared absorption (upper frame) and CD spectra (lower frame) of 2,2,2-trifluoro-1-phenylethanol, neat, with monochromator spectral bandpass 20 cm^{-1} (full width at half-height). The CD spectra show the raw data exactly as recorded. A fivefold reduction in bandpass causes only 8% change in the absorption band half-width. The CD zero has been displaced between (+), (±), and (−) measurements; the actual curves are indistinguishable at 3030 cm^{-1}.

of (+)-, (−)-, and (±)-I between 3130 and 2800 cm^{-1}. The samples used compare favorably[10] to material prepared previously by us.[11] Moreover, it has been established that the (+)-enantiomer has the S configuration.[12] The absorption spectrum of I shows a peak at 2920 cm^{-1}, which must involve primarily a C*–H stretch at the α-carbon atom.[13] The increasing absorbance near 3030 cm^{-1} arises from phenyl C–H stretching modes. Figure 1 shows that the C*–H band exhibits circular dichroism with $\Delta\epsilon/\epsilon = 6.5 \times 10^{-5}$. The rotational strength for this band is $+2 \times 10^{-44}$ esu^2 cm^2 for the (S)-(+) enantiomer; the dipole strength is 1.4×10^{-39} esu^2 cm^2.

The CD maxima in Figure 1 occur about 20 cm^{-1} higher in energy than the absorption maximum. Our calculations[1] show that this probably reflects a statistical weighting of the vibrational rotational strengths of various molecular conformations.

As shown in Figure 1, no CD is found, to present instrumental sensitivity, at the phenyl C–H stretching frequencies of I. This is not surprising, since these groups are well removed from the asymmetric center.

The second molecule in which we have detected vibrational optical activity, (R)-(−)-II, also possesses stretching modes involving a light atom attached to an asymmetric carbon (C*–H and C*–D). The CD and absorption spectra of (−)-II, synthesized as previously described,[14] reveal negative CD with $\Delta\epsilon/\epsilon = -2 \times 10^{-5}$ in the region of the C*–D stretch, 2204 cm^{-1}. The effect is small, so we are less certain of these data than

(10) Product of Burdick and Jackson Laboratories, Inc. Observed [α]$_D^{27}$ +24.9 and −21.6° (c 2, CCl$_4$). A sample prepared by us and verified to be 99+% enantiometrically pure (αD^{26} −41.39° (neat); lit[11] αD^{25} −41.18° (neat)) gave [α]$_D^{20}$ −25.1° (c 3, CCl$_4$). The infrared absorption spectrum of the commercial sample between 4000 and 600 cm^{-1} is identical with that of material prepared by Feigl and Mosher.[11]
(11) D. M. Feigl and H. S. Mosher, *J. Org. Chem.*, **33**, 4242 (1968).
(12) H. M. Peters, D. M. Feigl, and H. S. Mosher, *J. Org. Chem.*, **33**, 4245 (1968).
(13) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen, London, 1958.
(14) B. Stephenson, G. Soladie, and H. S. Mosher, *J. Amer. Chem. Soc.*, **94**, 4814 (1972).