200–220-nm region evidently reflects the chirality contribution to the carbonyl group by the pseudoaxial bond on the α' carbon.

For example, in Figure 3 only the initial portion of the negative long-wavelength π–π^* transition Cotton effect expected on the basis of the cisoid enone chirality rule[6a] for the left-handed enone chirality in 3β-acetoxy-5α-cholest-8(14)-en-15-one (**6**)[14] and the positive effect expected for the right-handed enone chirality in A-norcholest-5-en-3-one (**8**)[18] can be detected. The dominant lower wavelength Cotton effects exhibited by **6** and **8** are of opposite sign, in agreement with the allylic axial chirality approach.[19] Similar correlations extend (Table I) to cholest-5-en-4-one and cholest-4-en-6-one as well as to other steroidal conjugated enones of reasonably certain conformation.

Table I. 200–220-nm Region Cotton Effects of Steroidal Enones

Chromophore	α'-Chirality contribution	Obsd Cotton effect
4-En-3-one[a–c]	2βH (+)	+
B-Nor-4-en-3-one[c]	2βH (+)	+
5-En-4-one[c]	3αH (−)	−
4-En-6-one[c]	7αH (+)	+
5-En-7-one[a,c]	8βH (−)	−
8(9)-En-7-one[a,c]	6βH (+)	+
8(14)-En-7-one[c]	6βH (+)	+
8(9)-En-11-one[a]	12αH (−)	−
9(11)-En-12-one[a]	13βMe (+)	+

[a] Reference 7a. [b] Reference 7b. [c] Reference 7c.

As anticipated, this allylic axial chirality interpretation of π–π^* region Cotton effects is applicable to heteroannular transoid conjugated dienes[3,20] and to a variety of cyclic conjugated trienes and dienones, in addition to other cyclic conjugated dienes and enones. Results of these further studies will be reported shortly.

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[18] C. W. Shoppee and G. H. R. Summers, *J. Chem. Soc.*, 2528 (1952). We cordially thank Professor Shoppee for advice concerning the hypobromite oxidation of cholesterol (homogeneous conditions imperative) to the Diels acid used in the preparation of 8.

[19] In contrast to 6, 3β-acetoxy-5α-ergosta-8(14),22-dien-15-one[14] exhibits a substantial CD maximum (positive) only in the 220-nm region.

[20] The apparent "exception" of a steroidal 6,8(14)-diene to the transoid diene chirality rule (and hence to our approach) as suggested by ORD data[3] is not supported by CD measurements.

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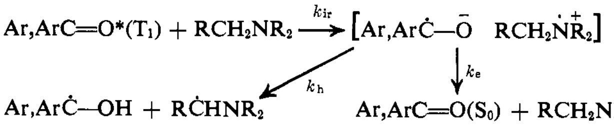
Effects of Polar Substituents on Photoreduction and Quenching of Fluorenone by Dimethylanilines[1]

Sir:

Photoreduction of aromatic ketones by aliphatic amines is characterized by moderately high quantum yields and low sensitivity to diffusion-controlled quenchers and to concentration of amine.[2] These reactions may proceed by rapid charge-transfer interactions,[2–5] for which rate constants, k_{ir}, may exceed $10^9\ M^{-1}\ \text{sec}^{-1}$, followed either by transfer of α hydrogen and formation of radicals, k_h, or by charge destruction and quenching, k_e (eq 1). Quantum yields would be



(1)

proportional to the fraction $f = k_h/(k_h + k_e)$, the rate constant for abstraction of hydrogen, $k_H = fk_{ir}$. It is of interest to examine effects of polar substituents on k_{ir} and on f. We report now on photoreduction and quenching of fluorenone by para-substituted dimethylanilines. Fluorenone is photoreduced by tertiary amines[6–8] in hydrocarbon solution, and this reaction, unlike that of benzophenone,[2] is not complicated by light-absorbing transients.

The dimethylanilines were obtained commercially or prepared by methylation of the corresponding anilines, and after purification had physical properties corresponding to literature values. Fluorenone was from Eastman, mp 83°. *trans*-Stilbene was from Pilot Chemicals, mp 124°. Aliquots, 3 ml, were degassed and irradiated in Pyrex under argon in 1-cm square tubes fitted with Teflon stopcocks, either on a turntable by a G.E. H-85-A3 lamp fitted with Corning 7380 filters, or by a Bausch and Lomb 38-86-01 monochromator at 405 nm. Analyses for fluorenone were made at 405 nm. Quantum yields were determined at 405 nm by ferrioxalate actinometry.[9] The pinacol, mp 182–185°, was obtained in essentially quantitative yield from photoreduction of fluorenone by dimethylaniline and by *p*-carbethoxy- and *p*-methyldimethylanilines. Solutions of 0.003 *M* fluorenone and 0.003–0.01 *M* dimethylaniline in benzene were irradiated on the turntable, and rates were converted to quantum yields. Linear plots of $1/\varphi$ *vs.* inverse concentration of amine[10] lead to intercepts, $k_{ir}/\varphi_{isc}k_H$, in which φ_{isc} is the quantum yield for formation of triplet,[11] ~0.93. The ratio of slope to intercept is k_d/k_{ir}, where k_d is the rate constant for self and solvent deactivation of the triplet. Solutions of 0.003 *M* fluorenone, 0.01 *M* dimethylaniline, and 0.001–0.01 *M* stilbene were irradiated on the turntable. Linear plots of the ratio of unquenched to quenched rates against concentration of quencher have slope = $k_q/(k_{ir}(\text{Am}) + k_d)$. Values of k_{ir} were based on k_q =

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[1] This work was supported by a predoctoral fellowship under Title IV NDEA, and by the U. S. Atomic Energy Commission, Grant No. AT(30-1)2499.

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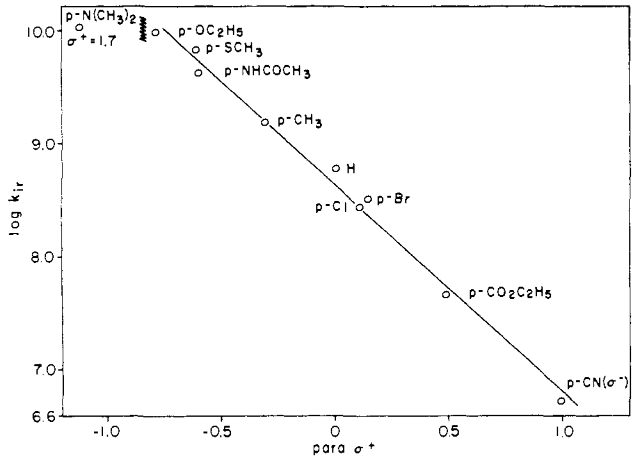
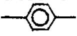


Figure 1. Interaction of fluorenone triplet with para-substituted dimethylanilines.

$3.6 \times 10^9\ M^{-1}\ sec^{-1}$.[12] Results are summarized in Table I.

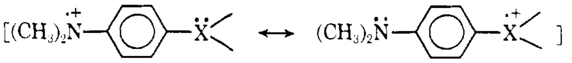
Table I. Photoreduction and Quenching of 0.003 *M* Fluorenone by Para-Substituted Dimethylanilines, X——$N(CH_3)_2$, in Benzene

p-X	Quantum yield[a]	k_H/k_{ir}[b]	k_{ir}, $M^{-1}\ sec^{-1}$	σ^+
-CN	0.09	0.11	5.4×10^6	+1.00[c]
$-CO_2C_2H_5$	0.12	0.17	4.7×10^7	+0.48
-Br	0.23	0.28	3.3×10^8	+0.15
-Cl	0.31	0.34	2.8×10^8	+0.11
-H	0.44	0.52	6.0×10^8	0.00
$-CH_3$	0.60	0.64	1.6×10^9	−0.31
$-SCH_3$	0.29	0.31	6.7×10^9	−0.60
$-OC_2H_5$	0.35	0.37	9.6×10^9	−0.78[d]
$-NHCOCH_3$	~0.02		4.1×10^9[e]	−0.60
$-N(CH_3)_2$	~0.02		1.6×10^{10}[e]	−1.70

[a] Observed quantum yields for photoreduction of fluorenone by 0.01 *M* dimethylanilines. [b] The fraction $f = k_h/(k_h + k_e)$, intercept of plot of $1/\varphi$ *vs.* $1/c$ divided by φ_{isc}. [c] σ^- value for *p*-CN. [d] Value is for *p*-OCH_3. [e] Value of k_q, determined by use as quencher for photoreduction of fluorenone by dimethylaniline.

Values of k_{ir} are high, slopes of the inverse plots are small, and quantum yields at 0.01 *M* amine are little less than the extrapolated values. Values of k_{ir} range from $5 \times 10^6\ M^{-1}\ sec^{-1}$ for *p*-CN to $10^{10}\ M^{-1}\ sec^{-1}$ for *p*-$N(CH_3)_2$. A linear plot of log k_{ir} *vs.* σ^+ may be constructed, $\rho = -1.83$. This supports development of positive charge at N and the charge-transfer mechanism. Most of the values of σ^+ are based on development of positive charge at carbon α to phenyl.[13] The first and last members of the series are exceptional. For *p*-CN, σ^- fits the plot, indicating important stabilization of the ground state. *p*-$N(CH_3)_2$ lies off the plot since the rate has become essentially diffusion controlled and can no longer respond to increasingly negative σ^+.

Quantum yields for reduction pass through a maximum. They rise from 0.09 at *p*-CN to 0.60 at *p*-CH_3, as electron-attracting substituents decrease not only k_{ir} but also *f*, and favor quenching. Substituents with more negative values of σ^+ than methyl raise k_{ir} but enhance k_e. *p*-Ethoxy and *p*-methylthio show lower quantum yields while *p*-dimethylamino and *p*-acetamido hardly photoreduce and are very effective quenchers. Their high values of k_{ir} are determined by study of them as quenchers of the photoreduction of fluorenone by dimethylaniline. This quenching may result from stabilization of the cationic part of the CT complex by interaction with electrons of the second substituent.



Alternatively, conjugation of n electrons of two such substituents with the aromatic ring may allow the triplet to interact directly with and be quenched by the aromatic system. The quenching depends on or is enhanced by the presence of the two substituents, since the related monosubstituted compounds, acetanilide, phenyl methyl thioether, and phenetole, do not quench this reaction. However *p*-ethoxyacetanilide is an effective quencher, $k_q(k_{ir}) \sim 7 \times 10^8\ M^{-1}\ sec^{-1}$.

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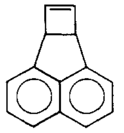
Naphtho[1,8]bicyclo[3.2.0]hepta-2,6-diene. Synthesis and Rearrangement to Pleiadiene[1]

Sir:

In conjunction with our interest in the chemistry of cyclobutane systems bonded to the peri positions of a naphthalene moiety,[2] we have synthesized naphtho-[1,8]bicyclo[3.2.0]hepta-2,6-diene (**1**). This compound,



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in addition to being useful for the synthesis of a number of derivatives of this ring system, has also interesting thermal and photochemical behavior.

Initially, the synthesis of **1** was effected in 2.4% overall yield from acenaphthylene as outlined in Chart I.[3]

The structures of adducts **2a** and **2b** were confirmed by conversion to the corresponding methyl esters and comparison of their nmr spectra with those reported by Rautenstruch and Wingler.[4] Identification of **1**, mp 118–119°, was made chiefly on the basis of its spectral data: nmr (CCl_4) τ 2.3–3.0 (multiplet, 6 H, aromatic), 3.72 (singlet, 2 H, -CH=CH-), and 5.39 (singlet, 2 H, benzylic CH); ir ($CHCl_3$) 2934, 1617,

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(1) The partial support of this research by the National Science Foundation (GP 13085) is acknowledged with pleasure.

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(3) Satisfactory analyses and spectral data were obtained for all key compounds.

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