pure **18**: 2.62 g (80%); bp 123–125 °C (10 mm) [lit.[1] bp 125–127 °C (11 mm)]; ^{1}H NMR ($CDCl_3$) δ 1.22 (t, 3 H, CH_2CH_3), 3.54 (q, 2 H, OCH_2) 4.64 (s, 2 H, $COCH_2$), 7.20–7.89 (m, 5 H).

α-Isopropoxyacetophenone (19). Use of isopropyl alcohol instead of ethanol in the last experiment yielded **19**: 1.49 g (42%); bp 87–88 °C (2 mm) [lit.[1] bp 87 °C (2 mm)]; ^{1}H NMR ($CDCl_3$) δ 1.20 [d, 6 H, $CH(CH_3)_2$], 3.62 (m, 1 H, $CH(CH_3)_2$], 4.61 (s, 2 H, $COCH_2$), 7.12–7.85 (m, 5 H).

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Notes

Stereoselection in the Hypervalent Iodine Oxidation of Chromium Tricarbonyl Complexes of Benzocyclanones

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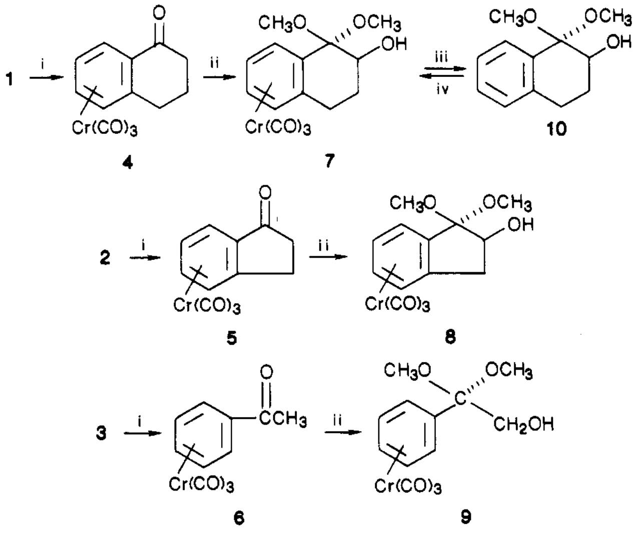
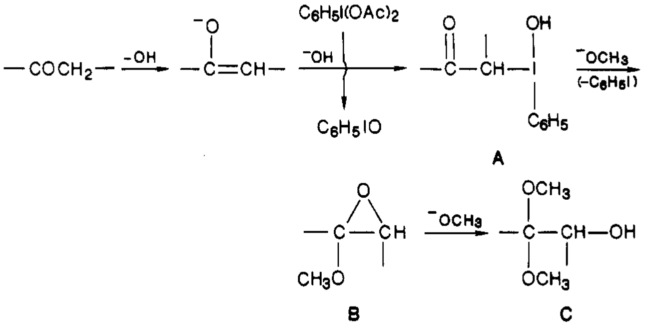
1-Tetralone (**1**) and 1-indanone (**2**) are achiral molecules that become chiral upon complexation with $Cr(CO)_3$: i.e., **1** → (η^6-1-tetralone)tricarbonylchromium(0) (**4**)[1] and **2** → (η^6-1-indanone)tricarbonylchromium(0) (**5**).[1a,b] **1** and **2** may be regarded more precisely as (pro)^1-chiral molecules.[2] The carbon atom at C2 is prostereogenic in the sense that introduction of a substituent by replacement of a hydrogen atom may yield proximate or distal orientations of that substituent with respect to the $Cr(CO)_3$ tripod. Furthermore, if the steric size of the group introduced at C2 is large, one might expect a high degree of stereoselection.[3] Since **1** and **2** have been resolved and the absolute configurations of the enantiomers are known,[1] stereospecific functionalization at C2 must yield a single diastereomer of known absolute configuration at C2, and subsequent disengagement of the ligand must likewise yield an enantiomer of known absolute configuration. α-Hydroxy dimethylacetal formation in the hyperiodination procedure for ketones[4] involves the intermediary introduction of the large $-I(OH)C_6H_5$ group α to the carbonyl group. This circumstance renders the reaction highly stereospecific.[5] The operation of a steric effect between $-I(OH)C_6H_5$ and the $Cr(CO)_3$ tripod was probed in the cases of **4** → **7**, **5** → **8**, and **6** → **9** with the expectation of realizing all the points of stereochemistry mentioned above.

Scheme I[a]



[a] Key: (i) $Cr(CO)_6$/diglyme; (ii) $C_6H_5I(OAc)_2$, KOH/MeOH; (iii) sunlight/air; (iv) $Cr(CO)_3(CH_3CN)_3$/dioxane.

Scheme II



The observed stereochemical course of **4** → **7** [OH proximate to $Cr(CO)_3$] can be rationized on the basis of the general mechanism that we determined for the hyperiodination of ketones to yield α-hydroxy dimethyl acetals.[4e,5]

Formation of **A** in the case of **4** or **5** must occur with addition of C_6H_5IO from the opposite face relative to the $Cr(CO)_3$ group because of a destabilizing steric interaction were these groups mutually proximate. Formation of **B** occurs with inversion of configuration at C2, thus placing the ring oxygen on the same face as the $Cr(CO)_3$.[5] The oxirane oxygen atom becomes the hydroxyl oxygen with retention of configuration at C2 in the displacement reaction **B** → **C** (Scheme II).

The molecular structure **7** as determined by X-ray diffraction is presented in Figure 1.[6] The stereochemical

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[1] (a) A preliminary communication of this work was reported: Moriarty, R. M.; Engerer, S. C.; Prakash, O.; Prakash, I.; Gill, U.S.; Freeman, W. A. *J. Chem. Soc., Chem. Commun.* **1985**, 1715. (b) Jaouen, G.; Meyer, A. *J. Am. Chem. Soc.* **1975**, *97*, 4667.

[2] Mislow, K.; Siegel, J. *J. Am. Chem. Soc.* **1984**, *106*, 3319.

[3] For a discussion of steric effects in addition reactions to some (arylcycloalkanone)tricarbonylchromium complexes, see: (a) Jackson, W. R.; Jennings, W. B. *J. Chem. Soc. B* **1969**, 1221. (b) Jackson, W. R.; Mitchell, T. R. B. *J. Chem. Soc. B* **1969**, 1228. (c) Trahanovsky, W. S.; Card, R. J. *J. Am. Chem. Soc.* **1972**, *94*, 2898. (d) Gracy, D. E. F.; Jackson, W. R.; McMullen, C. H.; Lompson, N. T. *J. Chem. Soc. B* **1969**, 1197. (e) Jaouen, G.; Top, S.; Laconi, A.; Couturier, D.; Brocard, J. *J. Am. Chem. Soc.* **1984**, *106*, 2207.

[4] (a) Moriarty, R. M.; Hu, H.; Gupta, S. C. *Tetrahedron Lett.* **1983**, *22*, 1283. (b) Moriarty, R. M.; John, L. S.; Du, P. C. *J. Chem. Soc., Chem. Commun.* **1981**, 641. (c) Moriarty, R. M.; Gupta, S.; Hu, H.; Berenschot, D. R.; White, K. B. *J. Am. Chem. Soc.* **1981**, *103*, 686. (d) Moriarty, R. M.; Hu, H. *Tetrahedron Lett.* **1981**, *22*, 2747. (e) Moriarty, R. M.; Hou, K. C. *Tetrahedron Lett.* **1984**, *25*, 691.

[5] Moriarty, R. M.; Prakash, O.; Freeman, W. A. *J. Chem. Soc., Chem. Commun.* **1984**, 927.

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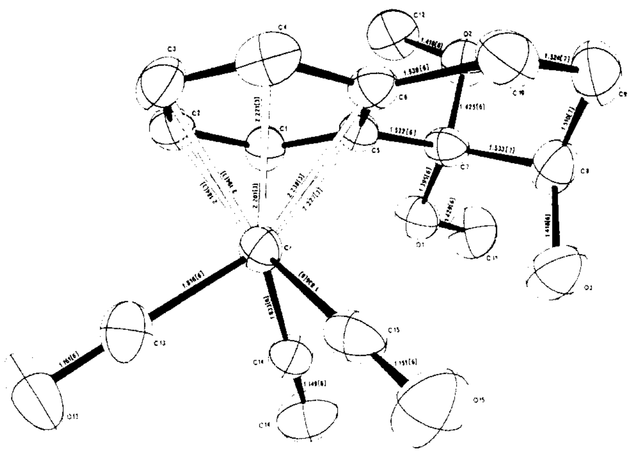
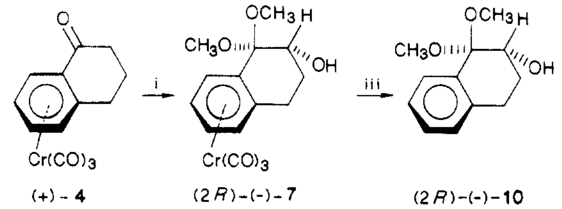


Figure 1. Perspective view (ORTEP) of **7** with bond distances; H atoms omitted for clarity.

Scheme III



relationships are confirmed by this determination. In addition, one notes that the $Cr(CO)_3$ tripod is neither eclipsed nor staggered with respect to the the arene ring carbon atoms. Sighting down the Cr–Z axis (where Z is the centroid of the benzene ring) the torsional angles are −17.6 (3), −17.0 (3), and −17.7 (3)°. The hydroxyl group oxygen atom O3 and the α-endo methoxyl oxygen atom are within hydrogen-bonding distance (2.833 Å).[7] The O(1)–C7–C8–O3 dihedral angle is 51.9 (3)°. Other dihedral angles (deg): O3–C8–C7–O1 = −51.94, O3–C8–C7–C5 = +68.0, O3–C8–C7–O2 = −173.13, C9–C8–C7–O7 = −173.02, C9–C8–C7–C5 = −53.08. These angles and the bond distances shown in Figure 1 compare well with those determined for (*endo*-2-methyl-1-indanol)tricarbonylchromium(0).[8]

Next, we complexed α-hydroxy dimethyl acetal **10** to $Cr(CO)_3$ to yield **7** as the only isolable organochromium product (**10** → **7**). Apparently the steric role of the hydroxyl group is not determinative, and perhaps even an attractive force exists between the OH group and $Cr(CO)_3$.

The final reaction sequence was carried through in the optically active series. Enantiomer **4**, $[\alpha]^{24}_{D}$ + 810° was prepared by the known procedure.[1] Hyperiodinative oxidation yielded diastereomer (2*R*)-**7**, $[\alpha]^{24}_{D}$ − 44° ($CHCl_3$), from which the free ligand was obtained by disengagement using sunlight in air[9] to yield (2*R*)-**10**, $[\alpha]^{24}$ −40° ($CHCl_3$),[10] of unknown optical purity (Scheme III).

This sequence illustrates the value of hyperiodinative oxidation of $Cr(CO)_3$-complexed ketones to yield synthetically useful and enantiomerically pure α-hydroxy dimethyl acetals or known configuration.

Experimental Section

Melting points were determined with a Thomas-Hoover capillary melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 727B spectrometer. NMR spectra were recorded on a Varian A-60. A Bruker WP-250 was used to record ^{13}C NMR spectra. Mass spectra were determined on a Perkin-Elmer GC–MS 5985 spectrometer. [(+)-1-Tetralone]tricarbonylchromium (**4**) was prepared by the method of Jaouen and Meyer.[1b]

(1,1-Dimethoxy-2-tetralol)tricarbonylchromium (7). Method A. (η^6-1-Tetralone)tricarbonylchromium(0) (**4**)[1b] (1.41 g, 0.005 mol) in 100 mL of CH_3OH was added dropwise to a stirred solution of KOH (0.84 g, 0.015 mol) in 25 mL of CH_3OH over a period of 15 min at 0 °C. After the solution was stirred for an additional 10 min, $C_6H_5I(OAc)_2$ (1.63 g, 0.0055 mol) was added portionwise and the resulting solution was stirred for 4-5 h at 0 °C and then overnight at room temperature. **7** separated out under these conditions as a yellow-green solid. The product was filtered and washed with water: 0.40 g; mp 171–176 °C. Addition of water to the filtrate gave an additional 0.40 g. The aqueous portion was extracted four times with CH_2Cl_2. The combined CH_2Cl_2 extracts were dried ($MgSO_4$) and concentrated to dryness in vacuo: yield 600 mg of **7**; mp 170–173 °C; pure yellow crystalline product; [1.4 g (80%); mp 176–179 °C; could also be recrystallized from Et_2O; ^1H NMR (acetone-d_6) δ 2.8 (4 H, s, CH_2's), 3.2 (3 H, s, OCH_3), 3.46 (3 H, s, OCH_3), 4.00–4.23 (1 H, m, C_2-H), 5.20–5.23 and 6.06 (4 H, m, aromatic protons); ^{13}C NMR (acetone-d_6) δ 234.3 (CO), 113.4, 96.5, 92.5, 86.6 (complexed aromatic), 66.1 (CHOH), 49.5, 48.8 (exo, endo), 26.0, 23.6 (CH_2's); IR (KBr, cm^{-1}) 3600 (OH), 3100, 3000, 1960, 1880, 1860 (C═O), 1520, 1500, 1450; MS, *m/z* 344 (M^+), 313, 288, 260, 229, 228, 226, 213, 212, 211, 210, 199, 199, 198, 196, 160, 145, 129, 117, 52.

Method B. (i) 1,1-Dimethoxy-2-tetralol (10). A solution of α-tetralone (5.84 g, 0.04 mol) in anhydrous methanol (30 mL) was added dropwise with stirring to a cooled solution (0 °C) of potassium hydroxide (7.02 g, 1.2 mol) in anhydrous methanol (150 mL). After the addition, iodobenzenediacetate (13.16 g, 0.044 mol) was added in small portions, maintaining the temperature inbetween 0 and 5 °C. The reaction mixture was stirred at 0–5 °C for 1 h and at 23–25 °C for 20 h. After the reaction, the solvent was removed on a rotating evaporator at 40 °C (22 torr). The remaining residue was mixed with water (150 mL) and extracted with ether (6 × 30 mL). The combined ether extracts were dried over anhydrous sodium sulfate and filtered, and the filtrate was evaporated on a rotating evaporator at 25 °C (20 torr). The remaining liquid was triturated with hexane. The solid obtained was recrystallized from hexane to give a white crystalline solid: 5.8 g (70%); mp 94–95 °C; MS, *m/z* 208 (M^+), 177, 165 (100), 163, 149, 119, 105, 91.

(ii) Formation of 7 from 10. A solution of **10** (4.5 mmol, 936 mg) in 40 mL of oxygen-free dioxane was added to solid $(CH_3CN)_3Cr(CO)_3$ (prepared by refluxing 1.1 g of $Cr(CO)_6$ in 40 mL of CH_3CN for 16 h) and refluxed for 24 h under N_2. Then, the mixture was filtered and the filtrate evaporated to dryness in vacuo. The crystalline residue was washed with hexane to yield 840 mg of **7** (60%). An additional 200 mg of **7** was obtained by concentration of the mother liquors. Recrystallization from CH_2Cl_2–hexane yielded pure **7** (mp 175–176 °C dec), essentially identical with material obtained in **4** → **7**.

(1,1-Dimethoxy-2-indanol)tricarbonylchromium (8). Compound **8** was prepared from (η^6-1-indanone)tricarbonyl-

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(6) Crystal data for **8**: triclinic; space group $P\bar{1}$; $a = 7.527$ (2), $b = 9.250$ (3), $c = 11.945$ (5) Å; $\alpha = 106.60$ (3), $\beta = 103.87$ (3), $\gamma = 103.65$ (2)°; $V = 731.2$ (4) Å^3; $Z = 2$; $D_c = 1.564$ g cm^{-3}. Data were collected on a Picker FACS-1 automatic diffractometer modified by a Krisel Control update package. A total of 1694 unique reflections with $F > 3.0\sigma(F)$ in the range $2.0 < 2\theta < 45.0°$ was used in the structure analysis. The data were corrected for absorption and secondary extinction. The structure was solved by direct methods and refined to $R = 0.0601$, $R_w = 0.0488$ using 204 variable parameters (Sheldrick, G. ACSHEL X, Programs for Crystal Structure Determination, University of Cambridge, 1975). The phenyl carbons were refined as part of a rigid hexagon. All hydrogens were placed at calculated positions [d(CC-H) = 1.08 Å] except the hydroxyl hydrogen which was located in a difference Fourier synthesis. All nonhydrogen atoms were refined with anisotropic temperature factors. Hydrogen atoms were divided into three groups and refined with just three isotropic temperature factors.

(7) Pimentel, G. C.; McClelland, A. D.; *The Hydrogen Bond*; Freeman: San Francisco, 1960. For example, OC·HBr, $R_{CBr} = 3.91$ Å, hydrogen-bond length 2.50 Å: Keenan, M. R.; Minton, T. K.; Legon, A. C.; Balle, T. J.; Flygare, W. H. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 5583.

(8) Gentric, E.; Le Borgne, G.; Grandjean, D. *J. Organomet. Chem.* **1968**, *155*, 207.

(9) Jaouen, G.; Dabard, R. *Tetrahedron Lett.* 1971, 1015.

(10) Rotation measurements were carried out on a Perkin-Elmer MC polarimeter.

chromium (**5**) in essentially the same way as **4** → **7**: yield 80%; mp 143–144 °C; NMR ($CDCl_3$) δ 2.4–3.1 (3 H, m, C_2- and C_3-H), 3.2 (3 H, s, OCH_3), 3.5 (3 H, s, OCH_3), 4.15 (1 H, m, OH), 5.1–5.6 (4 H, m, aromatic protons); MS, m/z 330 (M^+), 299, 274, 246, 228, 215, 198, 184 (100), 146, 132, 103, 52.

(2,2-Dimethoxy-2-phenylethano)tricarbonylchromium (9). (η^6-Acetophenone)tricarbonylchromium (**6**) was converted to α-hydroxy dimethyl acetal **9** essentially the same way as **4** → **7**: yield 60%; mp 96–98 °C; NMR ($CDCl_3$) δ 2.1 (1 H, t, OH), 3.3 (6 H, s, O CH_3's), 3.7 (2 H, d, CH_2), 5.0–5.8 (5 H, m, aromatic protons); MS, m/z 318 (M^+), 287, 262, 234, 203, 202, 186, 172 (100), 133, 114, 103, 100, 91, 52.

[(−)-1,1-Dimethoxy-2-tetralol]tricarbonylchromium [(2*R*)-7]. This reaction was carried out as above: mp 154–157 °C; yield 80%; $[\alpha]^{24}_D$ −44° (c 0.058, $CHCl_3$); IR (KBr, cm^{-1}) 3500 (OH str), 1960, 1880, 1865 (C≡O).

1,1-Dimethyl-2-tetralol (10). (1,1-Dimethoxy-2-tetralol)tricarbonylchromium (**7**; 70 mg, 0.0002 mol) was dissolved in anhydrous ether (200 mL) and was kept in sunlight for 6 h. The reaction mixture was filtered, and filtrate was washed with water (2 × 30 mL) and dried over anhydrous $MgSO_4$. After filtration it was concentrated in vacuo. The white semisolid product thus obtained was treated with hexane to obtain a white crystalline solid: 37 mg (90%); mp 93–94 °C; IR ($CHCl_3$ cm^{-1}) 3450 (OH str); NMR ($CDCl_3$) δ 2.0–2.9 (4 H, m, CH_2's), 3.03 (3 H, s, OCH_3), 3.35 (3 H, s, OCH_3), 4.2 (1 H, m, C_2-H), 7.0–7.8 (4 H, m, aromatic protons).

(−)-1,1-Dimethoxy-2-tetralol [(2*R*)-10]. This reaction was done as above: mp 91 °C; yield 80%; $[\alpha]^{24}_D$ −40° (c 0.096, $CHCl_3$).

Acknowledgment. The author thanks the Petroleum Research Fund, administered by the American Chemical Society, for support of the work.

Registry No. **1**, 529-34-0; **4**, 32735-36-7; (+)-**4**, 12110-42-8; **5**, 12153-72-9; **6**, 12153-11-6; **7**, 105561-11-3; (2*R*)-(−)-**7**, 103421-50-7; **8**, 105561-12-4; **9**, 103371-68-2; **10**, 83022-55-3; (2*R*)-(−)-**10**, 103239-03-8; $Cr(CO)_6$, 13007-92-6.

Supplementary Material Available: Table of X-ray positional parameters and temperature factors for **7** (2 pages). Ordering information is given on any current masthead page.

Charge-Transfer and Exciplex Pathway in the Photocycloaddition of 9-Anthracenecarbonitrile with Anthracene and Naphthalenes

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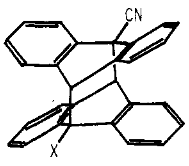
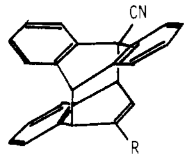
Received April 25, 1986

The role of excited complexes and of charge-transfer interaction in the 4 + 4 photocycloaddition of aromatic molecules is a subject of current interest.[1,2] Recent flash photolysis evidence suggests that the intermediate in the photocycloaddition (and photocycloreversion) of linked anthracenes has ion pair character in acetonitrile but not in diethyl ether.[3] From the preparative point of view it is known that an increase in the polarity of the medium enhances the yield of cross dimerization between 9-anthracenecarbonitrile (ACN) and 9,10-dimethylanthracene[4] and that the medium influences the head-to-head/head-to-tail ratio in the dimerization of 9-substituted anthracenes.[5] The formation of a head-to-head cross dimer from 9-methoxyanthracene and ACN is due to charge-transfer interaction.[6]

Chart I



1, X = CN
4, X = H



2, R = H
3, R = Me

We presently report the cross photodimerization of ACN with other aromatic molecules. The aim of the present study was twofold, viz. (i) to obtain mechanistic information by comparing the results with donors of different ionization potential and in different solvents, and (ii) to exploit charge-transfer excited complexes for the synthesis of new cross dimers, in particular anthracene–naphthalene 4 + 4 adducts, as these were previously obtained only by intramolecular cycloaddition from bichromophoric compounds.[1a,7]

Results and Discussion

Degassed solutions (2 × 10^{-3} M) of ACN in cyclohexane or acetonitrile were irradiated in the presence of aromatic donors at a concentration high enough to ensure that a significant portion of ACN singlet excited state is quenched. In the absence of quenchers ACN reacts efficiently under these conditions to yield the 4 + 4 dimer **1**[8] (Chart I), which precipitates out during irradiation.

Naphthalene is a poor quencher of ACN fluorescence (Table I, Stern–Volmer constant from steady-state measurements, $K_{SV} \leq 1.5$ M^{-1}). Irradiation in the presence of 0.05 M naphthalene yields an abundant precipitate of dimer **1**, but a new product is present in solution and is obtained in satisfactorily pure state by chromatography and recrystallization despite its limited stability (Table I). Spectroscopic properties (see Experimental Section) as well as reversion to ACN and naphthalene on melting or at room temperature both in solution (in days) or in the crystalline state (in months) allow unambiguous recognition of this compound as the cross dimer **2**.

Both 1- and 2-methylnaphthalene are better quenchers of ACN fluorescence than unsubstituted naphthalene. In the presence of the former compound the only product obtained is dimer **1**, but in the latter case this is accompanied by a certain amount of the cross dimer **3**, similar to product **2** as far as properties and stability are concerned.

This fits with the idea that substituents in position 1 hinder photocycloaddition and led to the examination of more 2-substituted naphthalenes. Compounds with electron-withdrawing substituents such as 2-cyano- or 2-carbomethoxynaphthalene do not appreciably quench ACN fluorescence nor influence dimerization to **1**.

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(1) For a review of the photodimerization of anthracene and related compounds, see: (a) Bouas-Laurent, H.; Castellan, A.; Desvergne, J. P. *Pure Appl. Chem.* **1980**, *52*, 2633. (b) Stevens, B. *Adv. Photochem.* **1971**, *8*, 161. (c) Cowan, D. O.; Drisko, R. L. *Elements of Organic Photochemistry*; Plenum: New York, 1976; p 37.

(2) For a discussion of the contribution of charge resonance to stabilization of an excimer, see: (a) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley Interscience: New York, 1970; p 327. (b) Gerhartz, W.; Poshusta, R. D.; Michl. J. *J. Am. Chem. Soc.* **1976**, *98*, 6427. (c) Ferguson, J. *J. Chem. Phys* **1958**, *28*, 765.

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(7) (a) Ferguson, J.; Puza, M. *Chem. Phys. Lett.* **1978**, *53*, 215. (b) Ferguson, J. *Chem. Phys. Lett.* **1980**, *76*, 398.

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