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TRANSANNULAR INTERACTIONS IN 1,8-(1',8'-NAPHTHALYL)NAPHTHALENE[1]

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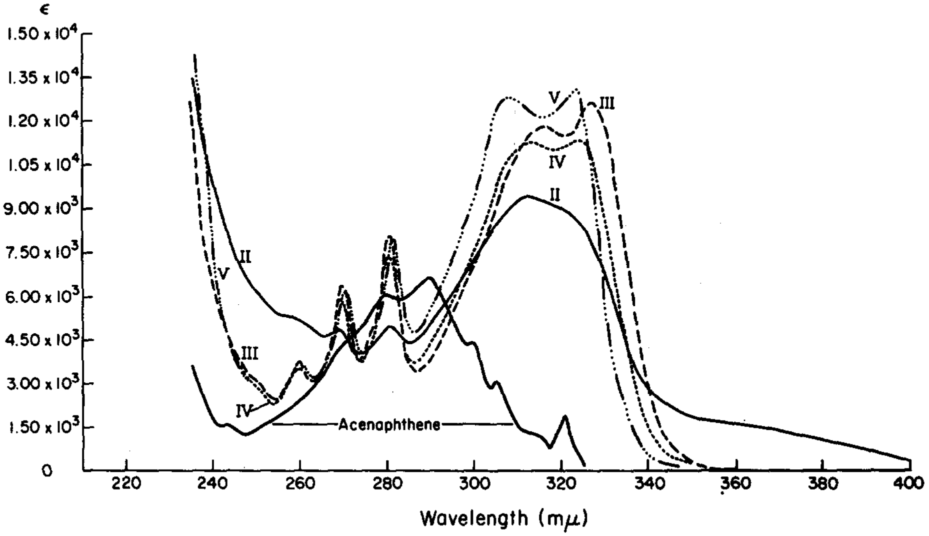
Examination of molecular models of 1,8-(1',8'-naphthalyl)naphthalene[2] (I) indicates the availability of a single, rather rigid conformation (II) free of distorted bond angles. Simultaneous conrotation or disrotation[3] of the carbonyl groups about the carbon-carbon single bonds, an operation serving to flatten or ultimately to invert the molecule, is inhibited by the considerable angle strain it introduces[4]. The compound should exist predominantly, therefore, in the conformation depicted (II), in which the carbonyl groups are held approximately 2.5 Å apart, close enough for significant transannular interaction. Below we report several reactions of II which reveal that formation of transannular carbon-oxygen or carbon-carbon bonds takes place with ease.

The first type of reaction leads to oxygen bridging and occurs most simply on hydration. Brief heating of an acetic acid solution of the diketone containing dilute hydrochloric acid converts it virtually quantitatively to hydrate III, (m.p. 321-323°[5], IR: 3501 and 3365 cm^{-1}(both strong), no carbonyl absorption). In contrast with other bridged ketone hydrates, III is exceptionally stable; it sublimes at 190°/0.06 mm without loss of water and is unaffected by p-toluenesulfonic acid and refluxing benzene in a water separator[6]. Furthermore, III is the only product isolated after two days' treatment of II with red phosphorus and hydriodic acid in acetic acid at 145° (55%) or from exposure of II to typical Clemmensen reduction conditions for 19 hours (52%). A second example of oxygen bridging is provided by hydride reduction. Treatment of II with excess lithium aluminum hydride in refluxing ether or, preferably, with excess sodium borohydride in dimethylformamide-isopropyl alcohol at room temperature leads to hemiketal IV, (62%, m.p. 300-304°[5], IR: 3338 cm^{-1}(strong), no carbonyl absorption). Models of III and IV appear strain-free[7]. Equilibrium in these reactions lies far on the side of the bridged compound. In the case of hydrate III this results presumably from carbonyl-carbonyl repulsion in the diketone form (II). Models of the hydroxy ketone corresponding to IV show clearly that the *endo*-hydroxyl is thrust into the π-cloud of the transannular carbonyl group, an unfavorable interaction readily relieved by hemiketal formation.

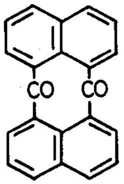
A second type of transannular reaction of diketone II involves carbon-carbon bond formation and may be exemplified by photoreduction. Irradiation[8] of a dilute solution of the compound in isopropyl alcohol gives pinacol V in 55% yield (melting point, mixture melting point, and infrared spectrum compared with those of an authentic sample[2]). A more striking reaction is that observed on attempted Wolff-Kishner reduction. Treatment of the diketone with hydrazine and potassium hydroxide in hot ethylene glycol gives chiefly (56%) the known[2] deep purple hydrocarbon VI, which was identified by comparison of its very simple infrared and quite complicated ultraviolet spectra and its melting point with those recorded[2,9]. The pathway shown or a similar one involving the bishydrazone is possible in this reduction, although the ease of oxygen bridging demonstrated above may point to some more complicated process here. The same product (VI) results in minute amount (0.3%, spectroscopically determined after alumina chromatography) on reduction of II with lithium aluminum hydride-aluminum chloride complex in ether.

In the figure are reproduced the ultraviolet spectra of compounds II, III, IV, and V in 95% ethanol. The absorption beyond 350 mμ unique to II is noteworthy, and may be attributable to transannular interaction of the carbonyl groups. Below 350 mμ the spectrum of II is similar to the others recorded, consistent with severely reduced carbonyl-ring interaction.[2] All the spectra, however, are abnormal for compounds possessing only a simple *peri*-dialkylnaphthalene chromophore, as can be seen from comparison with the quite typical curve of acenaphthene.[10]

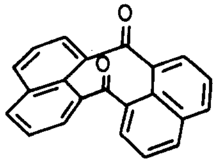
Further reactions of these and related compounds and the possibility of optical stability in a suitably substituted derivative of II[4] are under active investigation.



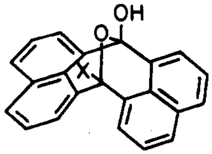
Ultraviolet spectra in 95% ethanol. All compounds show an additional maximum above 210 mμ ($\log \epsilon \sim 5$).



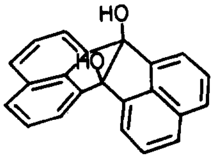
I



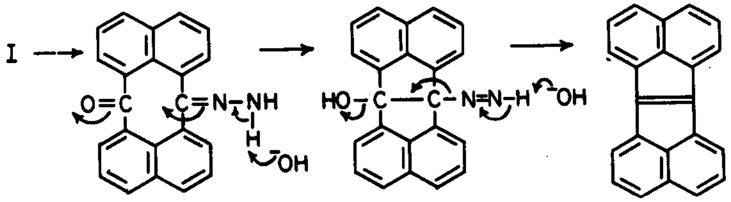
II



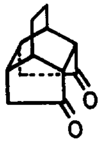
III, X = OH
IV, X = H



V



VI



VII

FOOTNOTES AND REFERENCES

1. This investigation was supported by National Science Foundation grant GB-137 and National Institutes of Health grant AM-02493.
2. R. L. Letsinger and J. A. Gilpin, *J. Org. Chem.* **29**, 243 (1964). These authors note that the carbonyl groups of I should not lie in the plane of either naphthalene ring. They report an ultraviolet spectrum (λ_{max}^{EtOH} 220 mμ (log ϵ 2.86), 280 (plateau, 3.05)) considerably different from that which we record in the figure.
3. R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.* **87**, 395 (1965).
4. If completed, such rotation leads to an equivalent but inverted conformation. In a monosubstituted derivative of I this inverted conformation is the enantiomer of the original array. 7,12-Dihydropleiadene and its simple derivatives provide a geometrically similar situation in which conformer stability is too low to permit optical resolution. *Cf.* P. T. Lansbury, J. F. Bieron, and M. Klein, *J. Am. Chem. Soc.* **88**, 1477 (1966).
5. This new compound gave satisfactory elementary analysis for carbon and hydrogen. Melting points were determined in sealed capillaries.
6. *Cf.* the behavior of VII, which hydrates on exposure to air and is dehydrated by sublimation at 170-180°. R. C. Cookson, E. Crundwell, R. R. Hill, and J. Hudec, *J. Chem. Soc.* 3062 (1964).
7. Crombie has recently commented on the effects of angle-strain on similar reactions in 7,12-dihydropleiadene-7,12-dione and related systems. M. E. C. Biffin, L. Crombie, and J. A. Elvidge, *J. Chem. Soc.* 7500 (1965).
8. Hanovia Lamp type L in a quartz immersion well with Pyrex filter was employed.
9. Letsinger and Gilpin (ref. 1) record for VI λ_{max}^{EtOH} 224.5 mμ (log ϵ 4.72), 232 (4.61), 244.5 (4.36), 291 (4.09), 385 (4.19), 404 (4.17). We find virtually identical maxima and intensities and also two weaker bands:

337 mμ (log ε 4.02) and 342 (4.03).

10. R. A. Friedel and M. Orchin, Ultraviolet Spectra of Aromatic Compounds, J. Wiley, New York (1951), Spectrum no. 212.