

STERIC EFFECTS IN COMPLEX COMPOUND FORMATION¹

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Polynuclear compounds are conveniently characterized by complex compound formation with picric acid, trinitrobenzene, trinitrofluorenone, or other polynitro compounds. The hydrocarbon and the polynitro compound form a molecular complex that is usually highly colored, sharp melting and readily dissociated in dilute solution by all types of solvents. Although the exact nature of the compound formation is still uncertain, it appears reasonable that the electron-poor (positive) centers at the nitrogen atoms interact with electron-donor (negative) centers on the hydrocarbon portion to form a complex that is held together by polar forces (1, 2). It is less likely that an ionic bond involving the complete transfer of an electron is involved, although claims have been made for this type of union (3). Electron-repelling groups on the hydrocarbon moiety usually enhance complex formation and have the opposite effect when substituted in the polynitro component (4). This partly explains the striking superiority of trinitrobenzene over picric acid as a complexing agent.

The present work stemmed from a review of molecular complex compound formation between picric acid and various tetracyclic hydrocarbons. It was found that many of the known facts regarding picrate formation in this series could be correlated by using the following assumptions:

(a) Picrate formation results from the interaction of the acceptor centers on one or more nitro groups of picric acid with one or more donor centers on the hydrocarbon.

(b) The melting point of the complex can generally be used as a criterion of the stability of the complex (4).

(c) The electron-rich portions of the hydrocarbon must be suitably spaced so that they coincide with the positive (nitrogen) centers in picric acid.³ The hydro-

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³ Some authors in discussing complex compound formation generalize that the ability of the hydrocarbon to enter into such complexes increases with the size of the aromatic ring. This is, however, not always the case even in the absence of steric hindrance. Naphthalene does not form a molecular complex with trinitrobenzene (Hertl and Bergk, *Z. physik Chem.*, **B33**, 319 (1936)) while naphthalene and anthracene readily do. It is the present author's opinion that the size and shape of the polynitro compound is also of importance; 2,4,7-trinitrofluorenone frequently forms complexes with hydrocarbons that do not complex with either picric acid or trinitrobenzene. In the tetracyclic series, the compact molecule of pyrene fits well over a picric acid molecule and this probably explains the fact that picrates of pyrene and its derivatives have high melting points. Although triphenylene is a somewhat larger molecule, the electron-rich centers in it are probably well distributed and permit easy accommodation of the positive centers of the picric acid molecule. Triphenylene, a very high-melting (199°) compound because of its symmetry, forms a picrate that is one of the highest-melting picrates (223°) known.

carbon and the picric acid molecules are then usually oriented in space in such a manner that the two components lie in parallel planes above and below each other.

(d) If, for some reason, the hydrocarbon is non-planar, the approach of the picric acid to the electron-donor centers may be inhibited. Complex compound formation is then made more difficult either because the non-planarity increases the distance through which the attractive forces must operate, or because the non-planarity decreases the number of resonance forms of the hydrocarbon and hence decreases the electron density at the electron-rich centers.

TABLE I
1,2-BENZANTHRACENES AND THEIR PICRATES

HYDROCARBON	M.P., °C.	M.P. OF PICRATE, °C.
1,2-Benzanthracene.....	159.5-160.5 ^a	141.5-142.5 ^b
3-Methyl-1,2-benzanthracene.....	155.9-156.9 ^c	153 ^d
4-Methyl-1,2-benzanthracene.....	126.2-127.2 ^c	149-150 ^e
5-Methyl-1,2-benzanthracene.....	160.0-160.6 ^c	165.8-166.3 ^f
6-Methyl-1,2-benzanthracene.....	150.5-151.5 ^g	152-153 ^g
7-Methyl-1,2-benzanthracene.....	183.0-183.6 ^c	159.0-159.4 ^h
8-Methyl-1,2-benzanthracene.....	117.4-118.4 ^c	159.5-160.0 ⁱ
9-Methyl-1,2-benzanthracene.....	138.6-139.6 ^c	115 ^d
10-Methyl-1,2-benzanthracene.....	140.2-140.80 ^j	173.5-174.0 ^f
1'-Methyl-1,2-benzanthracene.....	138 ^d	119 ^{d, k}
2'-Methyl-1,2-benzanthracene.....	150.7-151.7 ^c	180 ^d
3'-Methyl-1,2-benzanthracene.....	163.0-163.9 ^c	146.0-146.8 ^c
4'-Methyl-1,2-benzanthracene.....	194 ^d	139 ^d

^a Fieser and Hershberg, *J. Am. Chem. Soc.*, **59**, 2502 (1937). ^b Cook and Hewett, *J. Chem. Soc.*, 1408 (1933). ^c Newman and Gaertner, *J. Am. Chem. Soc.*, **72**, 264 (1950). ^d Cook and Robinson, *J. Chem. Soc.*, 505 (1938). ^e Cook, *J. Chem. Soc.*, 1592 (1933). ^f Fieser and Newman, *J. Am. Chem. Soc.*, **58**, 2376 (1936). ^g Cook, *J. Chem. Soc.*, 456 (1932). ^h Cook and Robinson, (*d*), reported that this picrate was too readily dissociated to be isolated. A sample of the pure hydrocarbon was secured from Dr. M. S. Newman and in our hands it readily formed a stable picrate, deep red needles from petroleum ether, benzene. Analysis by ultraviolet spectroscopy showed it to be a 1:1 complex. ⁱ Fieser and Johnson, *J. Am. Chem. Soc.*, **61**, 168 (1939). ^j Fieser and Newman, *J. Am. Chem. Soc.*, **58**, 2381 (1936). ^k This is a dimeric picrate; all the other picrates are monopicates.

Most of the above assumptions are either implied or explicitly stated in the work of other authors (5, 6, 7). The present work emphasizes the importance of steric factors and demonstrates that steric hindrance can lead to anomalies in picrate formation which may be explained by the inability of the hydrocarbon and picric acid to assume a close planar orientation. It is, of course, realized that the rigid application of the above assumptions leads to an over-simplification of the phenomenon of picrate formation especially since crystal forces are entirely neglected. Nevertheless specific examples of anomalies in picrate formation and detailed consideration of the data pertaining to picrate formation in two tetracyclic systems will indicate the usefulness of these assumptions.

Picrates of the methyl-1,2-benzanthracenes. Table I shows the melting points of the various monomethyl-1,2-benzanthracenes and their picrates.

Although the melting point of 1,2-benzanthracene picrate is 18° lower than that of the hydrocarbon, the melting points of the picrates of all twelve monomethyl 1,2-benzanthracenes are higher than the corresponding hydrocarbon with two exceptions. The exceptions involve substitution at position where

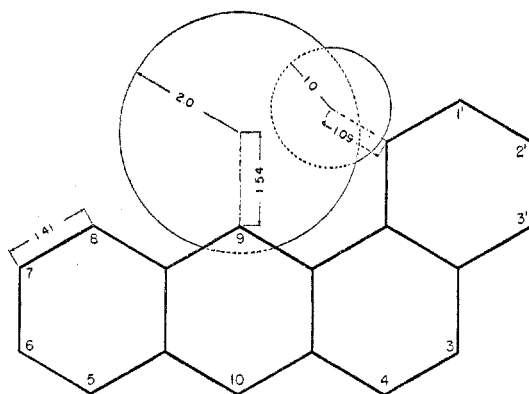


FIG. 1. PLANAR REPRESENTATION OF 9-METHYL-1,2-BENZANTHRACENE

TABLE II
BENZO[*c*]PHENANTHRENES AND THEIR PICRATES

HYDROCARBON	M.P., °C.	PICRATE, M.P., °C.
Benzo[<i>c</i>]phenanthrene.....	168 ^a	126-127 ^a
1-Methylbenzo[<i>c</i>]phenanthrene.....	141.4-141.9 ^b	none ^b
2-Methylbenzo[<i>c</i>]phenanthrene.....	80-81 ^c	118-118.5 ^c
3-Methylbenzo[<i>c</i>]phenanthrene.....	54-54.5 ^c	134-134.5 ^c
4-Methylbenzo[<i>c</i>]phenanthrene.....	65-66 ^c	107-108 ^c
5-Methylbenzo[<i>c</i>]phenanthrene.....	70.4-71.0 ^d	141.8-143.2 ^d
6-Methylbenzo[<i>c</i>]phenanthrene.....	77-78 ^c	112.5-113.5 ^c

^a Cook, *J. Chem. Soc.*, 2524 (1931); ^b Newman and Wheatley, *J. Am. Chem. Soc.*, **70**, 1913 (1948). ^c Hewett, *J. Chem. Soc.*, 1286 (1933). ^d Newman and Joshel, *J. Am. Chem. Soc.*, **62**, 972 (1940).

steric interference between a methyl group and hydrogen is possible. 9-Methyl-1,2-benzanthracene has a melting point of 138°, but its picrate (m.p. 115°) is by far the lowest-melting monopicate in the methyl-1,2-benzanthracene series. Figure 1 shows that the methyl group at the 9-position interferes with the hydrogen at the 1'-position. This overlap may prevent close approach of the picric acid molecule and weaken the stability of the complex. 1'-Methyl-1,2-benzanthracene, the other exception, forms a picrate in the ratio of two moles of picric acid to one mole of the hydrocarbon. This may be explained by assuming some type of non-planarity arising from steric interference between the methyl group

at 1' and the hydrogen at 9 which prevents or inhibits the approach of the picric acid molecule directly over the 1,2-benzanthracene nucleus. The hydrocarbon molecule, because of its lack of planarity, may function as two naphthalene nuclei each of which is capable of reacting with a picric acid molecule. The same explanation can be used to account for the fact that 9,10-dimethyl-1,2-benzanthracene alone, of all the known picrates of the dimethyl-1,2-benzanthracene series, forms a dipicrate (8).

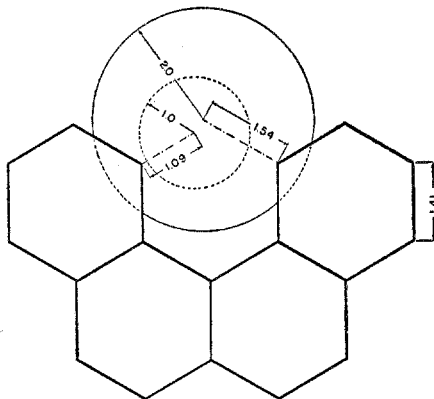


FIG. 2. PLANAR REPRESENTATION OF 1-METHYLBENZO[C]-PHENANTHRENE

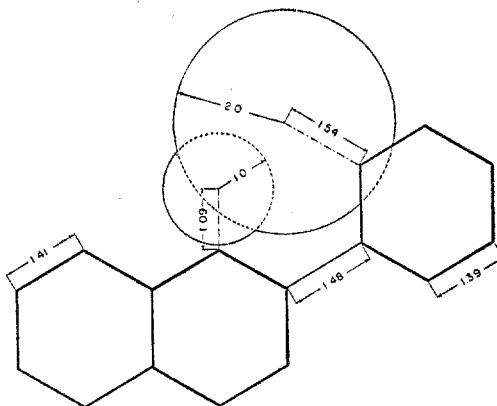


FIG. 3. PLANAR REPRESENTATION OF 2-O-TOLYLNAPHTHALENE

Picrates of the methylbenzo[c]phenanthrenes. All six possible monomethylbenzo[c]phenanthrenes and their picrates have been prepared. The melting points of the compounds are given in Table II. The picrates of all the compounds except the 1-methyl derivative behave in the expected manner. Attempts to prepare a picrate from 1-methylbenzo[c]phenanthrene were unsuccessful (9) although a complex with trinitrofluorenone could be prepared. The failure to secure a picrate is probably related to the non-planarity of the molecule arising from overlap at the 1 and 12 positions as shown in Fig. 2.

Other specific examples. *trans*-Stilbene forms a picrate, melting point 94°, but the *cis*-isomer fails to form a complex. Models show that in the *cis*-form, steric interference prevents the two phenyl groups from being in the same plane. In 1-phenylnaphthalene, coplanarity of the phenyl and naphthyl nuclei is inhibited (10); this molecule fails to form a picrate while 2-phenylnaphthalene, which can be completely planar, does form a picrate. On the other hand, substitution of a methyl group in the 2'-position of 2-phenylnaphthalene (2-*o*-tolyl-naphthalene) destroys the ability to form a picrate, although a trinitrobenzene complex can still be isolated (11). The methyl-hydrogen overlap and resulting resistance to planarity in 2-*o*-tolyl-naphthalene is apparent from Fig. 3. Although substitution of a methyl group on a ring usually enhances the donor characteristics of the hydrocarbon, the steric effect in this instance is a more powerful influence. The failure of 2-isopropenylnaphthalene to yield a picrate (12) while 2-isopropylnaphthalene forms one (13) is probably due to steric hindrance in the unsaturated compound.

SUMMARY

The importance of steric factors in complex compound (picrate) formation is demonstrated. Although substitution of a methyl group on the hydrocarbon usually enhances the ease of formation and stability of the picrate, if the methyl group is located where steric interference (methyl, hydrogen overlap) is possible, complex formation is often made more difficult, or the complex forms in other than a 1:1 ratio. The anomalous behavior is probably due to the non-planarity of the hydrocarbon molecule.

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