entrapment of the solvent was observed. The thiocyanato-(β- and γ-)-picolinenickel(II) complex compounds have been the only ones of many tested in this Laboratory which have so markedly exhibited this property.

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Methyl Affinities of Non-planar Aromatic Hydrocarbons

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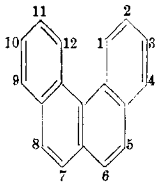
It was shown in a previous communication[1] that methyl radicals add to aromatic compounds, such an addition being initiated by reaction (1)

$$A + CH_3 \longrightarrow A{\cdot}CH_3 \qquad (1)$$

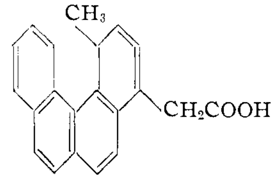
The relative rate constants of reaction (1), referred to as methyl affinities, were measured for a series of aromatic hydrocarbons, and it was found that their magnitudes are greatly affected by the structure of the aromatic compound. Thus, the following values were reported[1] for the methyl affinities of benzene, naphthalene, anthracene and naphthacene, namely: 1, 22, 820 and 9250, respectively.

Methyl affinities may be correlated to various properties of aromatic molecules; for example, it was shown by Szwarc[2] that logarithms of methyl affinities vary linearly with the singlet–triplet excitation energies; a similar relation was established by Coulson[3] for localization energies, while Matsen[4] correlated methyl affinities to electron affinities and ionization potentials. The correlation between the constitution of an aromatic molecule and its methyl affinity could be better understood by investigating systematically the effects of various structural changes on methyl affinity. In this communication, we shall deal with effects caused by the deviation of a molecule of an aromatic hydrocarbon from its planar configuration.

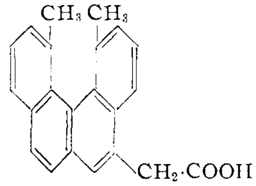
Certain aromatic hydrocarbons as, *e.g.*, some substituted benzo(c)phenanthrenes, can be caused to become non-planar as a result of intramolecular overcrowding.[5] The unsubstituted benzo(c)phenanthrene (I) has been shown to be non-planar in the solid state.[6] The non-planarity of substituted benzo(c)phenanthrenes is proved by partial resolution and facile racemization of 1-methylbenzo(c)phenanthrene-4-acetic acid[5] (II) and further evidence has been provided recently by resolution of 1,12-dimethylbenzo(c)phenanthrene-5-acetic acid (III) which has been shown to be optically stable, even at higher temperatures.[7] The increasing optical stability of these compounds provides evidence of increasing internal strain and hence increasing non-planarity of the molecules.



I



II



III

The methyl affinities of all of the methyl benzo(c)phenanthrenes, as well as of I and of 1,12-dimethylbenzo(c)phenanthrene, have been determined and are listed in Table I. The methyl affinities of the 2-, 3-, 4-, 5- and 6-methylbenzo(c)phenanthrenes are roughly the same and about equal to that of the parent hydrocarbon I. However, the methyl affinity rises somewhat in 1-methylbenzo(c)phenanthrene and considerably in 1,12-dimethylbenzo(c)phenanthrene. Since this order is that of increasing strain due to intramolecular overcrowding,[8] it appears that an increase in departure from a coplanar structure for aromatics leads to an increase in methyl affinity. Probably the deformation increases the localization of the electrons which are usually delocalized in aromatic rings and hence leads to increased availability of electrons for reaction with free radicals.

TABLE I

METHYL AFFINITIES OF BENZO(c)PHENANTHRENE AND ITS DERIVATIVES

Solvent, toluene; $T = 85°$.

Benzo(c)phenanthrene[a]	Mole %	CH_4/CO_2	k_{II}/k_I	Methyl affinity
Non-substituted	2.1	0.562	8.5	64
2-Methyl-	4.3	.506	7.2	55
3-Methyl-	4.3	.475	9.1	68
3-Methyl-	4.0	.475	9.8	73.5
4-Methyl-	4.3	.467	9.7	73
5-Methyl-	4.3	.496	7.8	58.5
6-Methyl-	4.3	.508	7.1	53.5
6-Methyl-	4.0	.474	9.9	74
1-Methyl-	4.3	.405	14.4	108
1-Methyl-	3.1	.459	14.2	107
1,12-Dimethyl-	4.0	.330	24.5	184
1,12-Dimethyl-	4.0	.330	24.5	184
1,12-Dimethyl-	4.0	.333	24.2	181

[a] The numeration of positions in benzo(c)phenanthrene is shown in I.

JOINT CONTRIBUTION FROM
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