# CHEMICAL REACTIVITIES OF ARYLCYCLOALKENES. VI. MOLECULAR COMPOUNDS OF TRINITROFLUORENONE WITH SOME SUBSTITUTED NAPHTHALENES. II[1, 2]

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In a previous publication (1) we reported apparent equilibrium constants, measured spectrophotometrically, in glacial acetic acid solution for the reaction of complex formation

$$\text{hydrocarbon} \;+\; \text{TNF} \;\rightleftarrows\; \text{hydrocarbon} \cdot \text{TNF},$$
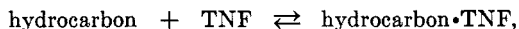
where TNF is 2,4,7-trinitrofluorenone and the hydrocarbons (substrates) studied were I–IV, 1-methylnaphthalene (XI), and 2-methylnaphthalene (XII). The present paper is concerned with (a) an extension of these studies to the substrates naphthalene (XVII) and substituted naphthalenes VI–IX as well as those bearing the groups 1-vinyl (V), 2-vinyl (X), 1-bromo (XIII), 2-bromo (XIV), 1-acetyl (XV), and 2-acetyl (XVI) and (b) a general interpretation of the results (Table I) for all 17 compounds.

For R = H: I   II   III   IV
For R = CH₃: VI   VII   VIII   IX
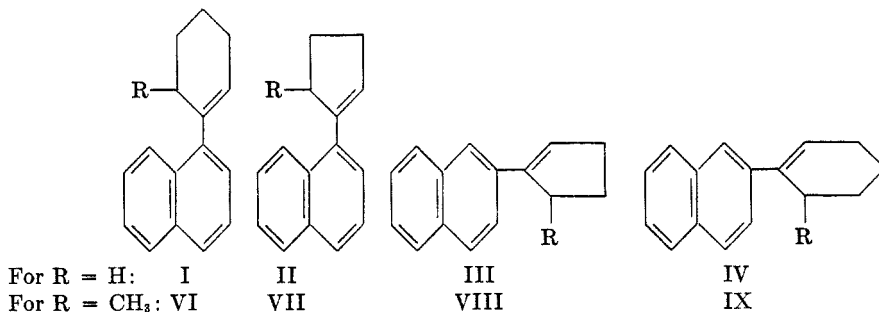
In general the procedure followed was exactly the same as used before (1) but with small modifications. For those complexes which had low extinction co-efficients at 460 mμ, somewhat different wavelengths (where absorbances were larger) were generally used for measurements of the K's. Equimolar stoichiometry for the complexes was checked for VI–IX by the method of continuous variations (1) and was assumed *ipso facto* for V, X, and XIII–XVII by conformance of the plotted data to linearity as shown by the equation derived for such a composition [cf. equation 1 and Fig. 4 in ref. (1)]. In addition isolable crystalline 1:1 complexes have been obtained for V, X, XV, and XVI and have been reported for VIII (2), XIII, XIV, and XVII (3).

[2] Presented at the Northwest Regional Meeting of the American Chemical Society, Richland, Washington, June, 1954. For paper V on arylcycloalkenes see ref. (5). For paper I on TNF complexes see ref. (1).

TABLE I

APPARENT STABILITY CONSTANTS FOR 1:1 MOLECULAR COMPOUNDS OF NAPHTHALENE AND SIXTEEN SUBSTITUTED NAPHTHALENES WITH 2,4,7-TRINITROFLUORENONE

Compound or Substrate	Substituent[a]	K^b (stability)	ϵ^c at 460 mμ	G-Factor[c]	Angle of Twist in Substrate[d] $\theta°$ min.	Sidewise Projections in Substrate[e]
XVII	None	17.0 ± 0.6[f]	661[g]	0	0	±0.50
XI	1-Methyl	27.5 ± 0.7	1000	0	0	±0.76
XII	2-Methyl	27.6 ± 0.8	988	0	0	±0.76
XIII	1-Bromo	21.5 ± 0.6[h]	470[i]	−0.3	0	±0.59
XIV	2-Bromo	16.0 ± 0.5[h]	440[j]	0	0	±0.59
XV	1-Acetyl	17.9 ± 0.6[f]	244[k]	−0.2	42 or 65	+0.68, −1.18
XVI	2-Acetyl	14.7 ± 0.6[f]	275[l]	0 (?)	0[m]	±0.91[n]
V	1-Vinyl	28.7 ± 0.8	1000[o]	+0.1	36 or 42	+0.65, −0.88
X	2-Vinyl	31.5 ± 1.0	993[o]	0	0	±0.50
I	1-Cyclohexenyl	16.0 ± 0.9	748	+2.2	52 or 80	+1.18, −1.26
IV	2-Cyclohexenyl	50.5 ± 1.5	1060	0	0	+0.97, −1.09[w]
II	1-Cyclopentenyl	21.6 ± 0.6	922	+2.0	44	—[p]
III	2-Cyclopentenyl	64 ± 2	1010	0	0	—[q]
VI	1-(Methylcyclohexenyl)	9.5 ± 0.5	758	+4.3	78[r] 85[s]	+1.06, −1.59[r] +1.15, −1.79[s]
IX	2-(Methylcyclohexenyl)	16.3 ± 0.8	921	+2.1	0[r] 4[s]	+0.94, −1.38[r] +0.91, −1.59[s]
VII	1-(Methylcyclopentenyl)	15.2 ± 1.3	568	+3.2	50–75[t]	—[u]
VIII	2-(Methylcyclopentenyl)	29.7 ± 1.9	979	+1.2	0[t]	—[v]

[a] On naphthalene ring. [b] In glacial acetic acid solution at room temperature. [c] See text for explanation of this term. [d] Many of these values are taken from Table II, ref. (5). Others are measured similarly. The available range for $\theta_{min.}$ is 0–90°. Where two values are given, $\theta_{min.}$ will depend on the direction in which the substituent is turned with respect to the naphthalene ring. [e] Based on the scale 1.00 = thickness of the naphthalene ring. Values were obtained from visual measurements on Fisher-Hirschfelder-Taylor models by means of a ruler, and represent minimum projections above and below the central geometric plane of the naphthalene ring. These values do not always correspond to $\theta_{min.}$. [f] Based on measurements at 430 mμ. [g] $\epsilon_0 = 1310$ at 430 mμ. [h] Based on measurements at 440 mμ. [i] $\epsilon_0 = 860$ at 440 mμ. [j] $\epsilon_0 = 900$ at 440 mμ. [k] $\epsilon_c = 908$ at 430 mμ. [l] $\epsilon_c = 980$ at 430 mμ. [m] Free rotation of the acetyl group is possible provided appropriate rotation of the methyl portion accompanies it. [n] Assuming some hindrance to free rotation in the molecule. [o] Average results from measurements at 430, 460, and 490 mμ. [p] Assumed to be less than for I. [q] Assumed to be less than for IV. [r] For methyl group in the polar position. [s] For methyl group in the equatorial position. [t] Estimated on bases of data for other compounds. [u] Assumed to be less than for VI. [v] Assumed to be less than for IX. [w] Owing to the flexibility of the cyclohexenyl ring toward broadside deformation, these values are probably somewhat too high.

Inspection of Table I shows a number of pertinent details. Thus, K is independent of the position of substitution on the naphthalene ring for the methyl group only. In every other case, except for the bromo and acetyl groups, 2-substitution fosters greater stability than does 1-substitution. Methylation of the naphthalene nucleus enhances stability—in agreement with general observations

on such complexes (4). The bromo and acetyl groups confer less stability than does the methyl group though not necessarily less than for hydrogen. The vinyl group, despite its available π-electrons, is little more effective than the methyl group in increasing stability. The order of stability in the 2-isomers is cyclopentenyl > cyclohexenyl > vinyl, while in the 1-isomers it is altered to vinyl > cyclopentenyl > cyclohexenyl. The methylcycloalkenyl groups, in which the methyl portion is essentially electrically insulated from interaction with the double bond or the naphthalene ring, all produce less stability (most notably for the 2-isomers) than do the corresponding cycloalkenyl homologs. A model which, we believe, successfully correlates these observations with our previous proposals on (a) the relative geometries of the substrate and TNF (such that a 2-substituent is susceptible to more extensive overlap by the TNF molecule than is a 1-substituent) and (b) aspects of coplanarity in the molecules as based on ultraviolet absorption spectra (5) and Fisher-Hirschfelder-Taylor molecular models (*vide infra*) is detailed in subsequent paragraphs.

In accordance with the generally accepted model for polynitroaromatic molecular compounds (at least of 1:1 type)[3] interaction between the addenda occurs largely by way of Lewis acid-base attraction between the aromatic nuclei of the substrate (base) and the complexing agent (acid) to form a preferentially planarly parallel configuration. Stability would, thence, be expected to increase with the increasing availability of π-type electronic charge principally in the naphthalene nucleus (and *vice versa*)—irrespective of whether such availability resulted from an inherent polarity in the substrate itself (as would be principally the case for the methylnaphthalenes) or from polarization of the substrate by the TNF (as would, for example, be more important in the case of the vinylnaphthalenes). Since in these studies the polarizing agent (TNF) and the aromatic nucleus (naphthalene) of the substrate remain the same, one can assign such combined electrical influences to the relative electron-donating tendencies (E_d) of the substituents. In general, inherent electron-donating tendencies would not be expected to be manifested in our complexes, due to two major modifying circumstances. First, the overlap of the π-electrons of a 2-substituent (but not of a 1-substituent) by TNF would prevent a maximum drain of electrons into the naphthalene ring. Second, lack of coplanarity, as occurs particularly in most of the 1-isomers, would interfere with electron drift in either direction (*i.e.* into or out of the naphthalene ring).

Stability of the complex would also be expected to decrease with F-strain, of the type proposed by Brown, *et al.* (6) except that the region of acid-base interaction would be an area of general overlap instead of a specific electron pair. In our complexes the source of such F-strain would lie in the projection of a substituent above or below the plane of the naphthalene ring to a sufficient distance and in an appropriate direction so as to inhibit optimal juxtaposition of the TNF and the naphthyl moiety. Such a projection might result from non-coplanarity in the substrate and/or a bulkiness of the substituent. The F-strain should cause the complex to forsake the planar parallel configuration for a tilted or wedge-shaped structure, to undergo interplanar sliding so as to retain planar paral-

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[3] *Cf.* (1) and references given therein.

lelism but with decreased overlap, to assume an interplanar distance which is greater than the optimum value, or to attain some alternate structural mutation.

Only four of the substrates studied can be considered both entirely free of F-strain and also demonstrative of an inherent electron-donating tendency for the substituent. These are naphthalene, the methylnaphthalenes, and 1-bromonaphthalene. To facilitate comparisons, however, let us consider the substrates III, IV, X, XII, XIV, XVI, and XVII—all of which can be considered coplanar (Table I), flat (*i.e.* without hindering projections), and similar in conditions of overlap. For these molecules then, the K's should be direct measures of the E_d-values of the substituents, in the reasonable order Ac(14.7) < Br(16.0) < H(17.0) < Me(27.6) < vinyl(31.5) < cyclohexenyl(50.5) < cyclopentenyl(64).[4] From previous arguments on electrical effects one also has methylcyclohexenyl = cyclohexenyl and methylcyclopentenyl = cyclopentenyl in E_d for our olefins. We now define a geometric factor, G, by means of the equation

$$G = \frac{E_d}{K} - 1,$$

where G will be the relative summation of all variations in stability of the TNF complex resulting from a change in the substrate away from a 2-substituted coplanar flat structure. In the case of VIII or IX the G-factor may be considered a measure of the out-of-the-plane projection by the methyl portion of the cycloalkenyl group (latter group coplanar with naphthalene). Correspondingly for I, II, VI, and VII the G-factor measures the combined results of a shift of the substituent to the 1-position and non-coplanarity—with steric (as based on the fact that the K's are less than for 1-methylnaphthalene) as well as polar effects attendant thereto. More precisely for VI (where perpendicularity of the substituent to the naphthalene nucleus is essentially complete) the change from K = 27.5 for 1-methylnaphthalene to K = 9.5 for VI may be considered as due entirely to F-strain. The negative G-factor for XIII is ascribed to a more effective electromeric drain of electrons into the ring from the non-overlapped 1-bromo atom than from the overlapped 2-bromo one. Perhaps this same effect almost serves to compensate for the limited deviation from coplanarity in the 1-vinyl derivative V; while it overcompensates for non-coplanarity effects in XV, where the acetyl substituent is less susceptible to polarization by the TNF.

<div align="center">EXPERIMENTAL[5]</div>

The preparation and purification of *olefins* VI–IX were described elsewhere (2). C.p. *naphthalene* was recrystallized twice from methanol, m.p. 79.5–80.5°. *1-Bromonaphthalene*

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[4] The difference in order of E_d from that of cyclohexenyl < cyclopentenyl < vinyl ascribed to the conjugative tendencies C_t of the groups (5) may be due to an opposite direction of polarization in the substrate for the cases of (a) TNF complex formation and (b) the Diels-Alder reaction [where Bachmann and Deno (7) have proposed that the terminal carbon of the vinyl group is the "most potentially nucleophilic"]. The transformation cycloalkenyl → cycloalkylidene [cf. (8)] would still prevail irrespective of the direction of polarization.

[5] Melting points are uncorrected. Microanalyses were performed by Micro-Tech Laboratories, Skokie, Illinois.

(Distillation Products Industries) was recrystallized from absolute ethanol as the picrate, recovered by dissociation, and distilled, b.p. 101–102° (1.9 mm.). *2-Bromonaphthalene*, prepared from β-naphthylamine,[8] was recrystallized from methanol (Norit A) to constant m.p., 56–57°. *1-Acetylnaphthalene* (DPI blue label) was purified as for 1-bromonaphthalene, b.p. 133–134° (3.4 mm.). *2-Acetylnaphthalene* (DPI white label) was used without further purification, m.p. 54–55°.

1-Vinylnaphthalene. To a 25-ml. Claisen flask, evacuated to 2–3 mm. pressure, immersed in a bath maintained at 210–220°, and containing a mixture of 2 g. of potassium bisulfate and 2 ml. of Hyvac oil, was added (at such a rate that even distillation was maintained) 15 g. of molten methyl 1-naphthyl carbinol (from 1-naphthylmagnesium bromide and acetaldehyde). The contents of the receiving trap (kept at 20–30°) were converted to the picrate which was recrystallized to constant m.p. 105–106° [reported (9) 101–102°] (yield 50–60% based on carbinol), dissociated chromatographically (10), and distilled as a colorless liquid, b.p. 100–101° (3.7 mm.) [reported (9) 115–116° (3–4 mm.)].

2-Vinylnaphthalene. Methyl 2-naphthyl carbinol, from low-pressure catalytic hydrogenation *via* Adams' platinum of a pretreated (refluxing with Raney nickel) ethanolic solution of 2-acetylnaphthalene, was dehydrated according to the aforementioned procedure, yield of picrate (after recrystallization to constant m.p. 91–92° as yellow needles from methanol) 30–36% (based on the carbinol). After chromatographic dissociation, distillation (b.p. 95–96° at 2.1 mm.), and two recrystallizations from methanol the product was obtained as flakes, m.p. 66–67° [reported (11) 65–66°].

TNF molecular compounds were prepared by admixture of equimolar quantities of V, X, XV, or XVI and TNF in glacial acetic acid and recrystallization of the precipitate from the same solvent to constant m.p.: *1-vinylnaphthalene•TNF*, orange-red rods, 134–136°; *2-vinylnaphthalene•TNF*, yellow crystals, 133–134°; *1-acetylnaphthalene•TNF*, yellow crystals, 125–126°; and *2-acetylnaphthalene•TNF*, yellow needles, 132–133°.

Anal. Calc'd for $C_{12}H_{10} \cdot C_{13}H_5N_3O_7$: C, 63.97; H, 3.22; N, 8.95.

Found 1-vinylnaphthalene•TNF: C, 63.70; H, 3.30; N, 8.97.

Found 2-vinylnaphthalene•TNF: C, 63.93; H, 3.22; N, 8.96.

Calc'd for $C_{12}H_{10}O \cdot C_{13}H_5N_3O_7$: C, 61.86; H, 3.12; N, 8.66.

Found 1-acetylnaphthalene•TNF: C, 62.54; H, 3.33; N, 9.09.

Found 2-acetylnaphthalene•TNF: C, 62.32; H, 3.24; N, 9.00.

The apparatus, procedure, and handling of data for use of the method of continuous variations and for the determinations of K were exactly the same as before (1), except for some change in certain cases in the wavelength used to measure K. Such alterations and the data obtained are given in Table I.

SUMMARY

1. Naphthalene and ten substituted naphthalenes have been shown to form 1:1 molecular compounds with 2,4,7-trinitrofluorenone in glacial acetic acid at room temperature.

2. Apparent stability constants for these complexes and six others (1), determined *via* spectrophotometry, are interpreted in terms of relative electron-donating tendencies of the substituents and geometric factors.

3. Four new crystalline TNF complexes were prepared.

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[8] We are indebted to Dr. Leonard Miller of the University of Illinois who furnished us the excellent directions of T. W. Shackleton for this conversion *via* the customary Sandmeyer procedure.

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