2-t-Butyl-1-nitropyrene and 2,7-Di-t-butyl-1-nitropyrene, Sterically Severely Hindered Aromatic Nitro Compounds

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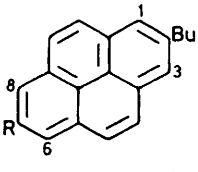
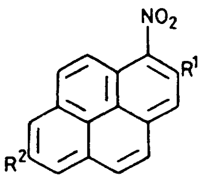
Nitration of 2-t-butylpyrene and 2,7-di-t-butylpyrene leads to nitro derivatives which show an extremely weak interaction between the nitro group and the aromatic π-system; the orientation of the nitro group prevents this group from conjugation with the π-system, leading to an unperturbed pyrene electronic spectrum.

During our studies on pyrene and its derivatives[1] related to their biological and environmental effects, we were interested as to whether a bulky group in position 2 would influence the electrophilic reactivity of the system. Treatment of 2,7-di-t-butylpyrene[2] (**1a**) with HNO_3 (1 equiv.) in acetic acid yielded 2,7-di-t-butyl-1-nitropyrene (**2a**) in pure form (75%); analytical data were in agreement with the structure. Surprisingly, however, this system shows properties that are unusual for an aromatic nitro compound. First, the electronic spectrum corresponds with that of the non-nitrated (**1a**). Secondly, in the ^1H n.m.r. spectrum the *peri* proton (10-H) displays an unexpectedly large (1.0 p.p.m.) upfield shift, with respect to the *peri* proton in 1-nitropyrene. Thirdly, in the i.r. spectrum the NO_2 stretching vibrations are shifted towards larger wavenumbers (58 cm^{-1}).

These observations can be explained by the 2-t-butyl group and the *peri* proton forcing the nitro group to adopt a perpendicular orientation relative to the π-system, thereby also causing a slight stretching of the $C(1)-NO_2$ bond. The nitro group then cannot be conjugated with the π-system, giving an unperturbed pyrene electronic spectrum for (**2a**). The upfield shift of the *peri* proton resonance is caused by the same steric effect (due to the magnetic anisotropy of the nitro group). That the presence of a single *ortho* t-butyl group is not sufficient to induce these dramatic effects is demonstrated by the electronic properties of 1,4-di-t-butyl-2-nitrobenzene[3] and 2-t-butyl-nitrobenzene.[4]



(**1**) a; R = Bu^t
b; R = H



(**2**) a; R^1 = R^2 = Bu^t
b; R^1 = Bu^t, R^2 = H
c; R^1 = H, R^2 = Bu^t

As a further consequence, the perpendicular orientation of the nitro group leads to a low electron-accepting capacity, as is shown by the ability of (**2a**) to be further nitrated to provide the 1,3-dinitro- (33%) as well as the 1,6- and 1,8-dinitro (33% each) derivatives. In contrast, the nitration of 1-nitropyrene gives a negligible amount of 1,3-dinitropyrene.[5]

In order to generalise our observations, we submitted 2-t-butylpyrene[6] (**1b**) to mono-nitration and obtained 40% of 2-t-butyl-1-nitropyrene (**2b**) and 60% of 2-t-butyl-6-nitropyrene (**2c**). Compound (**2b**) shows similar unusual properties to (**2a**), but (**2c**) behaves as a common aromatic nitro derivative, as expected. One of the products of the further nitration of (**2b**) is 2-t-butyl-1,3-dinitropyrene, another indication of the perpendicularity of the nitro group.

In view of these results we expect that many more highly hindered aromatic nitro compounds can be prepared easily and show analogous spectroscopic behaviour.

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