Tetrahedron Letters No. 18, pp 1561 - 1562.
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0040-4039/79/0429-1561$02.00/0

A TRIPLE-CLAMPED TRIPHENYLAMINE AND ITS RADICAL-CATION

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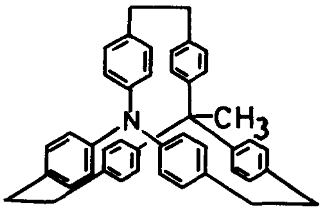
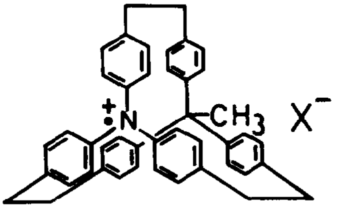
Earlier, we reported in detail on synthetic routes to triple-clamped triphenylethane and triphenylbenzene hydrocarbons 1). We now describe the synthesis and properties of the first representative of a triple-clamped radical of the above type, namely, radical-cation II derived from the bridged triphenylamine system I

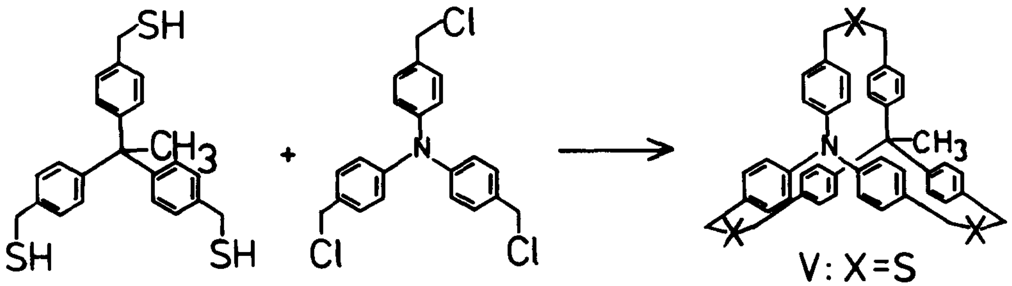


I



II

Reaction of 1,1,1-tris[4-(mercaptomethyl)phenyl]ethane (III) 1) with tris[4-(chloromethyl)phenyl]amine (IV) 1) under high dilution conditions gives the polycyclic trisulfide V, which is oxidized to sulfone VI. Subsequent pyrolysis of VI at $500^{\circ}C/10^{-6}$ Torr gives the desired amine I 2) (mp. 350°C, dec.) in approx. 9% yield, its purity being checked by tl-chromatography (R_F 0.46, chloroform/cyclohexane 1:1) 3). I is also characterised by high resolution mass spectrometry ($M^{\oplus\cdot}$ m/e calcd: 581.3083; found: 581 3096).



III IV V: X=S
VI: $X=SO_2$

The ^1H-NMR results [H(aromat.), $CHCl_3$: δ 5.7-6.1 (m), 7.0-7.5 (m)] show that the p-phenylene rings of the cyclic compound are fixed in propeller form in analogy to the bridged triphenylethane system [1].

The UV spectrum of the non-bridged tris(4-tolyl)amine (λ_{max}= 300 nm, log ε= 4 64, $CHCl_3$) shows no significant difference to that of the clamped molecule I (λ_{max}= 299 nm, log ε = 4 53, $CHCl_3$).

Oxidation of I in ether with $AgClO_4/I_2$ [4] leads to a violet-blue radical-cation, to which we ascribe structure II (X= ClO_4). The ESR spectrum shows a triplet with a coupling constant a_N= 10.7 G and a g value of 2.0027 G, which is not observed under similar conditions of measurement with tritolylaminium radical (a_N = 9.75 G, g= 2.0027 G). The smaller signal width (difference of 16 G) of the bridged radical points to a weaker coupling with the ortho and meta H-atoms. Since a stronger twist of the benzene rings in the bridged radical is improbable on sterical grounds, the weaker coupling may be due to a fixation of the pyramidal structure.

The UV spectrum of radical cation II (λ_{max}= 705 nm, log ε = 3.43, $CHCl_3$) shows a characteristic bathochromic shift of the long-wave maximum as compared with the open chain radical (λ_{max}= 670 nm, log ε = 3.43, $CHCl_3$) [5], lying thus only a little beneath the absorption maximum of the tris(4-methoxy)phenylaminium radical (λ_{max}= 715 nm). This may be due to a stabilisation of the electronically poorer excited state by transannular electron transfer through the opposite triphenylethane system.

Acknowledgement

We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for the support of this work.

References

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(Received in Germany 17 February 1979)