CONJUGATION IN THE 1,2,3-TRIPHENYLBENZENE SYSTEM

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Abstract—The relative reactivity of 1,2,3-triphenylbenzene (20 with reference to benzene), and the partial rate factors for NO_2 substitution in positions 4, 4′, and 4″ (18·6, 30, and 22·8 respectively) were determined by competitive nitration. The results suggest 'conjugation effect' as the factor responsible for the observed orientation and reactivity of the hydrocarbon in spite of its marked nonplanarity.

THIS research affords further chemical evidence of the effect of conjugation in 1,2,3-triphenylbenzene as a model of a highly nonplanar system. Although the conformation of this hydrocarbon is unknown, its UV spectrum suggests a greater departure from planarity than in *o*-terphenyl.[1]

From the evidence supplied by X-ray analysis the planes of the two outer rings of *o*-terphenyl are known to be twisted by about 45–50° out of the plane of the central ring.[2] The UV spectra—which reflect very sensitively interaction between the π-electron systems of the rings and, consequently, departure from planarity—have been studied extensively in *o*-terphenyl by Dale,[3] who interpreted the inflection at 252 mμ ($\varepsilon_{max} = 11400$, in hexane) as the main band of the full chromophore (λ_1), reduced in intensity and shifted towards the shorter wave range in comparison with *p*-terphenyl (λ_{max} 276 mμ, ε_{max} 32100) owing to the bent structure of *o*-terphenyl and steric hindrance. The minor band (λ_2; λ_{max}232 mμ, ε_{max} 26900, in hexane) is accordingly stronger, because it is allowed in the bent molecule. The great similarity of the spectra of *o*-terphenyl in solid state and in solution suggest only slight differences in interplanar angles.* Suzuki accepted Dale's assignment and, with the aid of the LCAO molecular orbital method, calculated the interplanar angles in the *o*-terphenyl molecule in solution as 43°.[4]

According to our measurements (in EtOH), the long-wave absorption band of 1,2,3-triphenylbenzene is strongly shifted towards the red as compared with that of the sterically less hindered isomers.[1]

The hypsochromic shift and absence in the spectrum of 1,2,3-triphenylbenzene of the inflection recorded from *o*-terphenyl and 1,2,4-triphenylbenzene suggests a greater restriction of conjugation, due to the steric interference of the three contiguous phenyl rings.

Failure of the conjugation effect of the phenyl substituents to affect the functional group in the central ring has also been demonstrated by our previously published

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* Dale[5] reached the same conclusion on finding the IR spectra of solid and dissolved *o*-terphenyl to be similar.

[1] D. Buza and W. Polaczkowa, *Bull. Acad. Polon. Sci., Ser. Sci. Chim.* **8**, 531 (1960).
[2] C. J. B. Clews and K. Lonsdale, *Proc. Roy. Soc.* A161, 493 (1937).
[3] J. Dale, *Acta Chem. Scand.* **11**, 650 (1957).
[4] H. Suzuki, *Bull. Chem. Soc. Japan* **33**, 109 (1960).
[5] J. Dale, *Acta Chem. Scand.* **11**, 640 (1957).

measurements of the dissociation constants of 3,4-diphenyl- and 3,4,5-triphenylbenzoic acids as well as 3,4-diphenyl- and 3,4,5-triphenylanilines.[6]

TABLE 1. UV SPECTRA OF ISOMERIC TRIPHENYLBENZENES, p-QUATERPHENYL AND DIPHENINYL IN EtOH

Compound	λ_{max} mμ	ε_{max}	λ_{max} mμ (inflection)	Lit.
p-Quaterphenyl	298	44000		1
1,3,5-Triphenylbenzene	252	58000		1
1,2,4-Triphenylbenzene	249	33000	ca. 270	1
1,2,3-Triphenylbenzene	239	33600	no inflection	1
Diphenyl	247·7	18050		7

In order to gain further information concerning mutual conjugation of rings in 1,2,3-triphenylbenzene we investigated orientation in electrophilic substitution of the hydrocarbon as exemplified in nitration.[8] From the mixture of the nitration products we isolated chromatographically three mononitro derivatives, which were identified by comparison of their m.ps and UV spectra with those of independently synthesized compounds.[9] In this way substitution was found to occur in positions 4, 4' and 4", which suggests conjugation as the factor responsible for orientation in 1,2,3-triphenyl-benzene molecule. Relevant evidence is supplied especially by substitution in position 4 in the central ring, and not in the sterically less hindered position 5, the former position being activated by conjugation with two, and the latter with only one phenyl ring. Absence of substitution in positions *ortho* is due to steric hindrance.
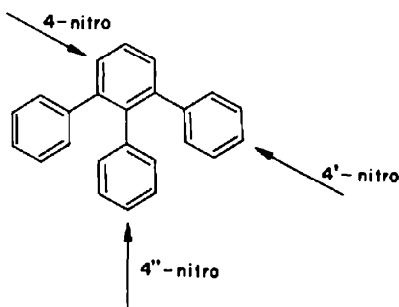

FIG. 1. Orientation in the 1,2,3-triphenylbenzene molecule.

The demonstrated *para* orientation points to conjugation in the system investigated and confirms the view of Böhm, who, anticipating possible complete inhibition of rotation in 1,2,3-triphenylbenzene, tried to isolate the stereoisomers of its suitably substituted derivatives and, having failed to detect them, assumed synchronized rotation of phenyl groups causing interconversion of the stereoisomers to be possible in the system investigated.[10]

A quantitative approach to the qualitative observations concerning orientation might yield unequivocal evidence of the influence of conjugation on the course of chemical reactions of systems having interplanar angles larger than 43° (in solution).

[6] W. Polaczkowa, N. Porowska and B. Dybowska, *Rocz. Chem.* **35**, 1263 (1961); *Ibid.* **36**, 41 (1962).
[7] H. Suzuki, *Bull. Chem. Soc. Japan* **32**, 1340 (1959).
[8] D. Buza and W. Polaczkowa, *Rocz. Chem.* **39**, 557 (1965).
[9] D. Buza and W. Polaczkowa, *Rocz. Chem.* **39**, 545 (1965).
[10] J. Böhm, *Rocz. Chem.* **35**, 821 (1961).

In the present work we have determined the relative reactivity of 1,2,3-triphenyl-benzene and calculated the partial rate factors for the positions at which substitution occurs according to the method of competitive nitration of 1,2,3-triphenylbenzene and benzene.

However, the method of competitive nitration calls for the same mechanism of the reactions of the compounds to be compared, irreversibility of the reaction in point, and arrestation of it at the stage of monosubstitution. Neither the mechanism nor the kinetics of 1,2,3-triphenylbenzene nitration have yet been investigated, but judging by the literature one may assume that all the essential conditions of investigations of competition have been met. In nitration, within a very wide range of conditions and for most aromatic compounds, the attacking reagent is the NO_2^+ ion. In our case both compounds were hydrocarbons, which ensured exactly similar mechanism of reaction.[11] Irreversibility was not in doubt, and the reaction was readily stopped at the stage of monosubstitution owing to the inactivating effect of the nitro group.

For competitive nitration, 1,2,3-triphenylbenzene and benzene were treated 48 hr in acetic anhydride solution with fuming nitric acid (1·505) at 25° in a thermostat. Such prolonged treatment was required by the high dilution due to the sparing solu-bility of 1,2,3-triphenylbenzene. The mononitro derivatives of benzene and triphenyl-benzene in the reaction mixture were determined by reduction in oxygen-free medium with a standard solution of $SnCl_2$,[12] and, with the aid of the method given by Ingold,[13] the relative reactivity of 1,2,3-triphenylbenzene was accordingly calculated as 20 (with reference to benzene). The relative reactivity of diphenyl, determined by the method of competitive nitration, is 40 (with reference to benzene).[14] The results are compiled in Table 2.

TABLE 2. RESULTS OF COMPETITIVE NITRATION OF 1,2,3-TRIPHENYLBENZENE AND BENZENE
(SUBSTRATES AND PRODUCTS GIVEN IN MMOLES)

Reagents	Experiments			
	I	II	III	IV
Benzene	150	150	100	100
1, 2, 3-Triphenylbenzene	10	10	10	10
HNO₃	8	8	8	8
Nitrobenzene	2·345	2·37	1·961	2·05
Nitrotriphenylbenzenes	2·645	2·515	2·88	2·78
Relative reactivity*	21·78	20·22	20·19	17·87
			mean value 20·01	

* For the method of calculation, see Ref. 13.

[11] C. K. Ingold, *Structure and Mechanism in Organic Chemistry* pp. 269–288. Cornell University Press, N.Y. (1953); P. B. D. de la Mare and J. H. Ridd, *Aromatic Substitution* pp. 57–77. Butter-worths, London (1959); M. A. Paul, *J. Amer. Chem. Soc.* **80**, 5329 (1958); C. J. Billing and R. O. C. Norman, *J. Chem. Soc.* 3885 (1961); G. W. Gray and D. Lewis, *J. Chem. Soc.* 5156 (1961).
[12] L. E. Hinkel, E. E. Ayling and T. M. Walters, *J. Chem. Soc.* 403 (1939).
[13] C. K. Ingold and F. R. Shaw, *J. Chem. Soc.* 2918 (1927).
[14] O. Simamura and Y. Mizuno, *Bull. Chem. Soc. Japan* **30**, 196 (1957); C. J. Billing and R. O. C. Norman, *J. Chem. Soc.* 3885 (1961).

Subsequently a part of the mixture of nitration products, separated from nitro-benzene, was chromatographed on alumina in order to determine the amounts of the isomeric mononitro derivatives formed in the reaction, i.e., 4″-nitro, 4′-nitro, and 4-nitro derivatives of 1,2,3-triphenylbenzene.

The mean relative reactivity of 1,2,3-triphenylbenzene and the percentages of the isomers served for calculations of the partial rate factors for the three positions of NO_2 substitution. The results are compiled in Table 3.

TABLE 3. ISOMER DISTRIBUTION AND PARTIAL RATE FACTORS FOR NITRATION OF
1,2,3-TRIPHENYLBENZENE IN ACETIC ANHYDRIDE

	Position of NO_2-group		
	4″	4′	4
Isomer distribution (%)	19·32	50·02	30·66
Partial rate factor	22·8	30	18·6

The experimental results show the reactivity of 1,2,3-triphenylbenzene in electro-philic substitution as exceeding that of benzene, but only one-half of that of diphenyl[14] (the interplanar angle of diphenyl in solution is according to Suzuki[5] about 23°). Considering that the electrophilic reagent attacks a molecule the more readily the greater the possibility of stabilization of cation in the transition state, the superior reactivity of triphenylbenzene over benzene can only be attributed to a mutual conjuga-tion of phenyl rings at the instant of reaction.

The partial rate factors for positions 4′, 4″, and 4 decrease in that order from 30 through 22·8 to 18·6.

The slightly higher reactivity of position 4′ than of 4″ suggests for the peripheral side rings a greater possibility of conjugation with the central ring than for the middle one owing to their spatial situation, extending the scope of conjugation. The reactivity of position 4 is the least and probably the resultant of the action of three factors: (1) the activating effect of the conjugation of the two phenyl substituents, $+E$; (2) the inactivating inductive effect of the substituents, $-I$; (3) steric hindrance. In effect, however, conjugation between the central ring and the two extreme phenyl rings pre-dominates, and the other factors only weaken it.

These facts deserve to be emphasized in connection with the evident nonplanarity of 1,2,3-triphenylbenzene. In spite of the nonplanarity and the sterical hindrance to conjugation of the central with the peripheral rings, this conjugation is possible tem-porarily in the transition state of the substitution reaction (conjugation of ring A with rings B and B′ at the expense of the perpendicular arrangement of ring C, or of ring A with ring C at the expense of the perpendicular arrangement of rings B and B′; see Fig. 2).
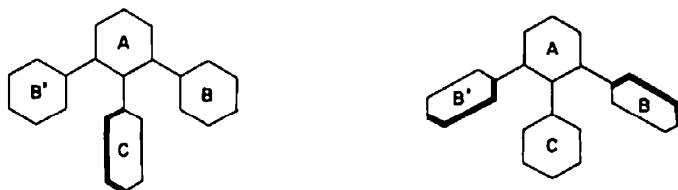

FIG. 2. The possibilities of the coplanar arrangement of the central ring (A) with the peripheral rings (B or C).

The attack of the electrophilic reagent, which creates a very great demand for the electrons essential for the reaction, seems to promote conjugation of the phenyl substituents with the reaction centre in the transition state, whereby conjugation becomes the factor determining the orientation and reactivity of 1,2,3-triphenylbenzene.

Thus the experiments afford unequivocal evidence of the effect of conjugation on chemical reaction in a strongly nonplanar polyphenyl system.

EXPERIMENTAL

Competitive nitration

The substrates for the experiments were used in following amounts:

Experiment	1,2,3-Triphenylbenzene	Benzene	HNO_3 (1·505)
I	3·06 g (0·01 M)	11·7 g (0·15 M)	0·35 ml (0·08 M)
II	3·06 g (0·01 M)	11·7 g (0·15 M)	0·35 ml (0·08 M)
III	3·06 g (0·01 M)	7·8 g (0·10 M)	0·35 ml (0·08 M)
IV	3·06 g (0·01 M)	7·8 g (0·10 M)	0·35 ml (0·08 M)

Triphenylbenzene and benzene were dissolved in 100 ml acetic anhydride (commercial product, C.P.) in a 3-necked flask fitted with a mechanical stirrer, reflux condenser, and thermometer. Nitric acid was added from a pipette with stirring and the temp kept at 15–20°. The flask was then kept in a thermostat for 48 hr at the temp of 25 ± 0·5°. The reaction mixture was poured into about 300 ml water, left overnight, and extracted 5 times with benzene. The extract was washed with $NaHCO_3$aq and water, and dried with $CaCl_2$. Benzene was removed by distillation under red. press. (Vigreux column) and the residue steam-distilled. Nitrobenzene was extracted from the distillate with benzene, the extract was dried with $CaCl_2$, the solvent was removed under red. press. (Vigreux column), and the nitrobenzene (NB) was dissolved in CO_2-saturated EtOH in a 25-ml volumetric flask and analysed for NO_2 content. The solid left after steam distillation was collected on a weighed filtering funnel and dried in a vacuum desiccator to yield in experiments I to IV respectively 3·19 g, 3·17 g, 3·17 g, and 3·14 g of reaction products (NTB). Weighed samples of the products were analysed for their contents of NO_2 groups by reduction with a standard solution of $SnCl_2$.

Determination of the content of nitrocompounds in the reaction products

Material and titrants. $SnCl_2·2H_2O$, A.R.; sublimed I_2, A.R.; KI, A.R.; soluble starch, A.R.; CO_2 from a Kipp generator. Distilled water was boiled several hr and saturated with CO_2 to remove air. EtOH was refluxed (10 hr) in a strong CO_2 current and saturated with CO_2 to remove aldehyde and air. A solution of $SnCl_2$ (ca. 2·5 N) was made by dissolving 283 g of $SnCl_2·2H_2O$ in 300 ml HCl (1·16) in a 1-litre volumetric flask and making up with deaerated water. The solution was stored under CO_2 in a dark bottle connected to a burette. A solution of I_2 in KI (ca. 0·6 N) was made by dissolving 76 g I_2 and 156 g KI in deaerated water in a 1-litre volumetric flask. The solution was kept in a burette with a tight chamber (ground in). A solution of starch was made by adding 2·5 g starch to 0·5 l. boiling water, and the whole boiled a few min, filtered, and saturated with CO_2.

The solution of I_2 in KI (5 ml) was diluted with distilled water, and titrated with a 0·1037 N $Na_2S_2O_3$ against starch as indicator. The I_2 solution was found to be 0·5977 normal (1 ml of the solution therefore was equiv. to 0·09962 mmole of NO_2).

The $SnCl_2$ solution (10 ml) was diluted with 50 ml water and titrated with I_2 solution against starch as indicator; the titer of the $SnCl_2$ solution was checked daily (the solution was 2·4864 N; hence, 1 ml of it was equiv. to 0·4144 mmole of NO_2).

A. *Determination of nitrobenzene content*

The apparatus for the reduction of the nitro compound consisted of a 0·5-litre 2-necked flask, a reflux condenser, and a gas-inlet tube reaching to the bottom of the flask and connected to a Kipp generator (CO_2). Before use, the apparatus was swept for 2 hr with CO_2 to remove air. Next, 10 ml ethanolic NB was pipetted into the flask, which was followed by 10 ml H_2SO_4 (1:1) and, from a burette, 10 ml 2·4864 N $SnCl_2$ solution in that order. The solution was slowly bubbled with CO_2

TABLE 4. RESULTS OF NITROBENZENE DETERMINATIONS

| Experiment | | Mlitres of iodine sol. used for titration | | | NO$_2$ in 10 ml of sol. in mmoles | Nitrobenzene total, in mmoles |
		BT	NB	BT-NB		
I	a	39·55	30·30	9·25	0·9214	2·30
						2·345
	b	40·30	30·70	9·60	0·9563	2·39
II	a	40·90	31·05	9·85	0·9713	2·45
						2·37
	b	40·55	31·35	9·20	0·9166	2·29
III	a	40·25	32·40	7·85	0·7820	1·955
						1·961
	b	40·45	32·55	7·90	0·7869	1·967
IV	a	40·20	32·20	8·00	0·7969	1·99
						2·05
	b	40·50	32·00	8·50	0·8467	2·11

(2 bubbles per sec) and heated on paraffin bath at 100–110° for 2 hr. During the reduction the condenser and the flask walls were flushed with two 5-ml volumes EtOH. Upon termination of the reaction the content of the flask was cooled to room temp in a CO$_2$ stream, 200 ml water was added, and the excess SnCl$_2$ backtitrated with I$_2$ solution against starch as indicator. Blank tests (BT) were made for each determination. The results are compiled in Table 4.

B. *Determination of the content of nitrotriphenylbenzenes*

The apparatus was as used for the reduction of nitrobenzene. A weighed sample of the substance to be analysed (NTB) was placed in the flask of the CO$_2$-swept (2 hr) apparatus, to which were added 10 ml EtOH, 10 ml H$_2$SO$_4$ (1:1), and, from a burette, 10 ml 2·4864 N SnCl$_2$ solution. The solution was slowly bubbled (2 bubbles per sec) with CO$_2$ and heated on a paraffin bath at 110–120° during 3 hr. During the reaction the condenser and the flask walls were flushed 3 to 4 times with 5-ml volumes EtOH. After the reaction the content of the flask was cooled to room temp in a stream of CO$_2$, 200 ml water was added, and the excess SnCl$_2$ was backtitrated with I$_2$ solution against starch as indicator. Blank tests (BT) were made for each determination. The results are compiled in Table 5.

TABLE 5. RESULTS OF DETERMINATIONS OF NITROTRIPHENYLBENZENES

| Experiment | | NTB, in grams | Mlitres iodine sol. used for titration | | | NO$_2$ content, in mmoles | Nitrocompounds total, in mmoles |
			BT	NTB	BT-NTB		
I	a	0·5417	39·40	34·85	4·55	0·4533	2·67
							2·645
	b	0·4917	39·35	35·30	4·05	0·4035	2·62
II	a	0·4626	39·10	35·90	3·20	0·3188	2·18
							2·515
	b	0·4744	40·00	35·70	4·30	0·4283	2·85
III	a	0·4479	39·15	35·10	4·05	0·4034	2·85
							2·88
	b	0·5094	40·00	35·30	4·70	0·4682	2·91
IV	a	0·5403	39·40	34·70	4·70	0·4683	2·72
							2·78
	b	0·5002	39·30	34·75	4·55	0·4533	2·845

Chromatography of the nitration products of 1,2,3-*triphenylbenzene*

The products of competitive nitration (NTB)—after steam-distillation of nitrobenzene—were chromatographed as in the experiments described previously.[*] A quantity of 3·79 g of the products were dissolved in 300 ml ligroin (b.p. 80–100°) with 40 ml benzene and fed on a column of 130 g Al_2O_3. The unchanged hydrocarbon was eluted with an exactly similar mixture of solvents, which also was used to elute the nitro derivatives, with the modification that the proportion of benzene was very gradually increased.

Chromatography afforded: (i) 1,2,3-triphenylbenzene, 2·5049 g (68·57%); (ii) mononitro derivatives—total, 1·0718 g (25·57%) including A. 4″-nitro-1,2,3-triphenylbenzene, m.p. 142–144° (0·2071 g) B. 4′-nitro-1,2,3-triphenylbenzene, m.p. 173–175° (0·5361 g) and C. 4-nitro-1,2,3-triphenylbenzene, m.p. 144–146° (0·3286 g); (iii) tars 0·1063 g (2·91%): (iv) balance, 3·683 g (97·05%). The various nitro derivatives were identified by comparing them with standard nitro compounds.[*]

The yields of the products of substitution in particular positions served for calculations of their percentages (isomer distribution) and partial rate factors for the positions.[*]

Position of NO_2-group	Isomer distribution (%)	Partial rate factor
4″	19·32	22·8
4′	50·02	30
4	30·66	18·6

[*] For the method of calculation, see Ref. 13.