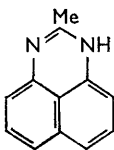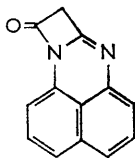# NOTES

1372. *New Observations on the Condensations of Malonic Acid with Naphthalene-1,8-diamine and o-Phenylenediamine*

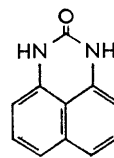By RICHARD F. SMITH and (MRS.) MARGARET M. HOLMER

SACHS [1] reported that naphthalene-1,8-diamine condensed with malonic acid to form 2-methylperimidine (I) and a by-product which was tentatively assigned the improbable structure (II). In our hands, several repetitions of the earlier work did not afford a product possessing the properties ascribed to (II). However, in addition to (I), we found that the reaction consistently gives small amounts of 2-perimidone (III).


[1] F. Sachs, *Annalen*, 1909, **365**, 112.

The formation of both (I) and (III) can be envisaged as occurring through a common intermediate (V) which could be formed by cyclisation of the acid (IV). Alternatively, (I) could be formed by cyclisation of *N*-acetylnaphthalene-1,8-diamine arising from decarboxylation of (IV) prior to cyclisation, or from direct condensation of the diamine with acetic acid.[1]
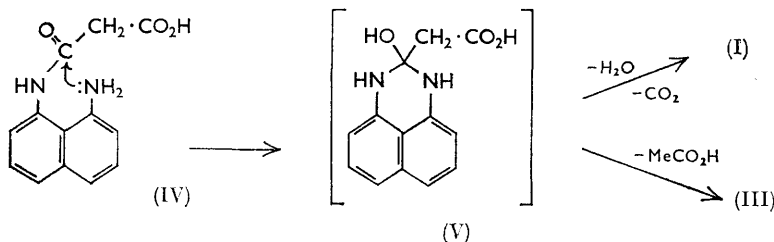
The n.m.r. spectrum of (III) indicated that the N–H protons are strongly deshielded. When determined in deuterated *NN*-dimethylformamide, the N–H resonance was observed as a singlet at γ −0·10 (2H). The aromatic protons were observed as two multiplets centred at τ 2·79 (4H) and τ 3·30 (2H).

Earlier workers[2] noted that the condensation of *o*-phenylenediamine with malonic acid in a 2 : 1 molar ratio gave the amide (VI) instead of the expected product (VII).
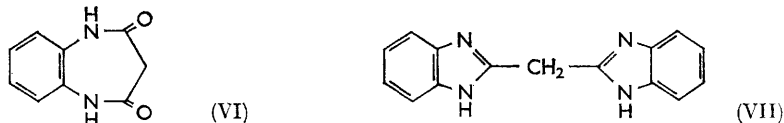
We have found that simple modifications (higher dilution and longer reaction times) of the procedure of Shriner and Boermans[2a] result in the formation of (VII) in 44% yield. Lane also prepared (VII) by the reaction of *o*-phenylenediamine with malonamide[3] and (VI).[4]

Experimental.—Melting points were taken on a Mel-temp. apparatus. The n.m.r. spectrum was determined with a Varian A-60 spectrometer, with tetramethylsilane as internal standard.

Typical condensation of malonic acid and naphthalene-1,8-*diamine.* An intimate mixture of the diamine (24 g.) and malonic acid (43 g.) was heated from 70° to 140° during 30 min. Heating was continued at 140—150° for 2 hr. The dark solid product was digested in boiling ethanol (450 ml.). Filtration of the hot solution gave 2-perimidone (III), m. p. 290—295° (2·7 g.). On cooling, the filtrate deposited an additional 2·0 g., m. p. 301—305°. Evaporation of the ethanol gave a solid that was digested with hot water (400 ml.). Filtration gave insoluble black material (2·6 g.) that afforded a small amount of 2-perimidone after crystallisation from acetic acid. Basification of the aqueous filtrate with ammonia afforded 2-methylperimidine (12·3 g.), m. p. 188—198°. The 2-perimidone formed needles, m. p. 306—307° (from acetic acid). Identity was established by m. p. and comparison of the infrared spectrum (KBr) with that of an authentic sample prepared in 70% yield by warming together a mixture of naphthalene-1,8-diamine (1·6 g.), potassium cyanate (2·0 g.), and acetic aid (20 ml.). Acetic acid was a more convenient solvent than hydrochloric acid[5] for the preparation of 2-perimidone.

Methylenebis-2-benzimidazole (VII) *dihydrochloride.* A mixture of *o*-phenylenediamine (10·8 g.), malonic acid (5·2 g.), and 4N-hydrochloric acid (120 ml.) was heated under reflux for 48 hr. with stirring. The resultant blue solution was filtered hot, treated with concentrated hydrochloric acid (10 ml.), and cooled to 0°, to give azure plates (7·0 g., 44%), m. p. 320—325° (decomp.). Basification of the filtrate with sodium carbonate afforded an insoluble brown solid (1·8 g.), m. p. >390°. The dihydrochloride crystallised from dilute hydrochloric acid as light azure plates, m. p. 328—332° (decomp., with prior darkening) [lit.,[3] 330—333° (decomp.)].

[2] (*a*) R. L. Shriner and P. G. Boermans, *J. Amer. Chem. Soc.*, 1944, **66**, 1810; (*b*) M. A. Phillips, *J.*, 1928, **172**, 2393; (*c*) R. Meyer *et al.*, *Annalen*, 1903, **327**, 1; 1906, **347**, 17; 1918, **415**, 29.
[3] E. S. Lane, *J.*, 1953 2238.
[4] E. S. Lane, *J.*, 1955, 1079.
[5] F. Sachs, *Annalen*, 1909, **365**, 315.

The infrared spectrum (KBr) was identical with that of a sample (yellow plates) prepared in low yield by the following variation of Lane's [3] procedure. An intimate mixture of o-phenylenediamine (5·4 g.) and malonamide (2·6 g.) was heated at 200° for 1 hr. The dark solid was boiled with 6N-hydrochloric acid (100 ml.) and the insoluble material filtered off. After treatment with charcoal, the cooled filtrate gave a product (1·5 g.) with m. p. 328—330° (decomp.). In our hands, the use of ethylene glycol as solvent gave only very small quantities of water-insoluble products.

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1373. *An Improved Preparative Method for Complexes* $[Pt_2Cl_4(R_3M)_2]$ *(M = P or As)*

By R. J. GOODFELLOW and L. M. VENANZI

BINUCLEAR compounds of platinum(II) of the type $[Pt_2Cl_4L_2]$ (I) are useful intermediates for the preparation of complexes containing mixed ligands. In a review of the methods available and their limitations,[1] the most useful method recommended for the preparation of complexes (I), where the uncharged ligand is a tertiary phosphine or arsine, consisted in melting together the mononuclear complexes $[PtCl_2L_2]$ with platinum(II) chloride. The success of this method depends on the mixture's remaining in the molten state until reaction is complete. It is, therefore, necessary to work at high temperatures when preparing high-melting compounds. This is not always possible as high temperatures cause excessive decomposition of the products. Furthermore, this method cannot be used when the starting materials, *e.g.*, $[PtCl_2(Ph_3P)_2]$ and $[PtCl_2(Me_3P)_2]$, decompose before melting. We report here a modification of this method which overcomes these difficulties by using a slurry of the reactants in a high-boiling hydrocarbon solvent. The hydrocarbon assists the reaction by keeping the reagents mobile, by lowering their melting points, and by dissolving them to a slight extent. The hydrocarbon is selected so that it refluxes at the required reaction temperature, and the insoluble reaction products are obtained by extracting the

Data on complexes $[Pt_2Cl_4(R_3M)_2]$

R₃M	Colour	Decomp. pt.	Hydrocarbon used *	Reaction temp.	Yield (%) A	B
1. Me₃P	Orange	200—210° ‡	Xylene + naphthalene	160°	— †	63
2. Et₃P	Orange	224—225§	Xylene	140	50	82
3. Ph₃P	Deep orange	270—280	Naphthalene	160	— †	70
4. Me₃As	Orange-red	220—225	Xylene + naphthalene	155	— †	79
5. Et₃As	Orange-red	208—209 ¶	Xylene	140	50	86

	Pt Found	Reqd.	P or As Found	Reqd.	C Found	Reqd.	H Found	Reqd.
1.	56·9	57·0	9·0	9·05				
2.	50·4	50·8	8·0	8·1				
3.	36·2	36·9	5·7	5·9	40·3	40·9	2·9	2·9
4.	50·3	50·5			9·6	9·3	2·4	2·35
5.	45·2	45·6						

A, Yield obtained using the method of Chatt and Venanzi.[1]   B, Yield obtained using the modified method.

* Enough naphthalene was added to xylene to obtain the desired reflux temperature.   † Could not be prepared by fusing together $[PtCl_2(R_3M)_2]$ and $PtCl_2$.[1]   ‡ Lit.,[1] decomp. 217—220°.   § Melting point (lit.,[1] 223—224°).   ¶ Melting point (lit.,[1] 208—209°).

[1] J. Chatt and L. M. Venanzi, *J.*, 1955, 2787, and references quoted therein.

diluent with light petroleum. The compounds prepared, and some data relating to them, are given in the Table.

Experimental.—Platinum [2] and phosphorus [3] were determined spectrophotometrically.

General method of preparation of complexes [$Pt_2Cl_4L_2$]. The complexes [$PtCl_2L_2$] (L = Me_3P, Et_3P, Ph_3P, Me_3As, and Et_3As) [1] (1 mole) and platinous chloride (1·05 moles) are finely ground in a mortar and transferred to a boiling-tube, and the hydrocarbon (or hydrocarbons) added to make a light slurry (*ca.* 10 c.c. of hydrocarbon for *ca.* 2—3 g. of reactants). The mixture is then heated in an oil-bath at the required temperature with occasional stirring. After cooling, the mixture is transferred to a Soxhlet thimble and washed well with light petroleum (b. p. 40—60°), using a continuous extractor. The product is then extracted with dichloromethane and recrystallised from either dichloromethane or chloroform. The triphenylphosphine compound could not be recrystallised and the crude product was purified by fractional extraction with dichloromethane. It was further characterised by reaction with *p*-toluidine.

trans-*Triphenylphosphine-p-toluidinedichloroplatinum.* *p*-Toluidine (55 mg.) was added to a suspension of [$Pt_2Cl_4(Ph_3P)_2$] (150 mg.) in dichloromethane (20 c.c.). The solid dissolved to give a greenish yellow solution which on evaporation gave the crude product. Pale yellow *plates* (180 mg., m. p. 250—251°) were obtained on recrystallisation from dichloromethane–benzene (Found: C, 47·7; H, 4·0; P, 4·8; Pt, 30·3. $C_{25}H_{24}Cl_2NPPt$ requires C, 47·25; H, 3·8; P, 4·9; Pt, 30·7%).

This work was carried out during the tenure of a D.S.I.R. studentship by R. J. G.

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[2] E. B. Sandell, " Colorimetric Determination of Traces of Metals," Interscience, New York, 1959, p. 726.
[3] G. Dyer, J. G. Hartley, and L. M. Venanzi, *J.*, 1965, 1293.

1374. *Association Constants from Contact Charge-transfer Spectra*

By J. E. PRUE

IN a recent Paper, Carter, Murrell, and Rosch[1] object to a model for charge-transfer interaction in solution proposed by Orgel and Mulliken.[2] One reason is the belief that this model assumes that the formation of " contact " complexes does not obey the mass-action law, in spite of the fact that, in a restatement of Orgel and Mulliken's proposals, Carter, Murrell, and Rosch write an equation (number 4) which is a statement based on a lattice model of the mass-action law for the complexes in question. Orgel and Mulliken's model merely postulates that there are two distinct equilibria. The first is the formation of a specific 1 : 1 complex between donor (D) and acceptor (A) molecules, whilst the second allows for a contribution to the charge-transfer spectrum by mere encounter between free D and A without any specific orientation or interaction (in the ground state) and without any restriction save that imposed by the co-ordination number of the liquid on the number of effective contacts a donor or acceptor molecule can make at any instant. The second has been called contact charge-transfer. It is, however, worth pointing out that, in terms of a simple model in which pair-interactions between D and A, whatever their nature, are described by a simple equilibrium D + A ⇌ DA (and it is on this that the so-called Benesi–Hildebrand[3] analysis is based), random collisions lead to an association constant significantly greater than many appear to appreciate.

Suppose that a pair of D and A molecules, the centres of which approach within a distance r to ($r + \Delta r$), give a charge-transfer absorption and are thereby counted as associated. The volume of the shell around a D molecule available to the centre of an associated A molecule is therefore $4\pi r^2 \Delta r$. In the absence of attraction between D and A, the fraction of molecules associated in this way $(1 - \alpha)$ will be equal to the ratio of the total

[1] S. Carter, J. N. Murrell, and E. J. Rosch, *J.*, 1965, 2048.
[2] L. E. Orgel and R. S. Mulliken, *J. Amer. Chem. Soc.*, 1957, **79**, 4839.
[3] H. A. Benesi and J. H. Hildebrand, *J. Amer. Chem. Soc.*, 1949, **71**, 2703.

volume of such shells to the remaining volume of the solution. With sufficient accuracy to obtain a rough value of the corresponding association constant K,

$$(1 - \alpha) = (4\pi r^2 \Delta r \times cV \times N)/V$$
$$K = (1 - \alpha)/\alpha^2 c = (1 - \alpha)/c \text{ if } \alpha \sim 1$$
$$= 4\pi r^2 \Delta r \, N,$$

where c is the stoicheiometric molar concentration of D and A, V is the volume of solution, and N is Avogadro's number.

A value of $r = 5$ Å is reasonable. An estimate of Δr is more difficult. Within a factor of 2 or 3, the " free volume " of liquids,[4] *i.e.*, the molar volume less the volume occupied by the molecules themselves, is about 0·5 ml. mole^{-1}. This means that in a liquid with cubical packing each molecule can move over a distance of $(0\cdot5 \text{ ml. mole}^{-1}/0\cdot6 \times 10^{24} \text{ mole}^{-1})^{\frac{1}{3}} = 0\cdot94$ Å with respect to a neighbour. As theory suggests [2] that charge-transfer absorption becomes possible at greater than van der Waals distances, it is reasonable to suppose that whenever D and A become neighbours without an interposed solvent molecule charge-transfer absorption can occur. We therefore set $\Delta r = 0\cdot94$ Å and obtain $K \sim 0\cdot2$ l. mole^{-1}. Association constants less than this are commonly reported as evidence for complex formation, *e.g.*, a value of 0·009 l. mole^{-1} for carbon tetrachloride and benzene in n-hexane.[5] Apart from the unreliability of the procedures used in evaluating such constants from experimental data, which have recently been critically discussed by Person,[6] it is clear that association constants of this magnitude evaluated from charge-transfer spectra do not provide any evidence for attractive forces between donor and acceptor molecules in the ground state in excess of the normal dispersion forces.

If D and A are ions, the expression for K must be multiplied by a Boltzmann factor to allow for the effect of Coulombic interactions. If the ions are oppositely charged, the equation for K becomes a simplified version of the familiar Bjerrum equation [7] for ion-pair formation. In favourable cases, *e.g.*, cupric chloride, a charge-transfer spectral effect can appear at degrees of association too low to have any effect on thermodynamic or conductance behaviour. Again the observation of such spectral effects must not by itself be regarded as evidence for specific interaction between ions in the ground state.

It is relevant to note here a suggestion [8] of Guggenheim's that the term " sociation " should be used to describe the degree of association in excess of that corresponding to random collisions.

These comments do not of course affect the issue of whether it is useful or necessary to endeavour to take account of the molecular nature of the solvent [1] in interpreting charge-transfer data.

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[4] J. F. Kincaid, H. Eyring, and A. E. Stern, *Chem. Rev.*, 1941, **28**, 301.
[5] R. Anderson and J. M. Prausnitz, *J. Chem. Phys.*, 1963, **39**, 1225.
[6] W. B. Person, *J. Amer. Chem. Soc.*, 1965, **87**, 167.
[7] N. Bjerrum, *Kgl. danske Videnskab. Selskab, Mat.-fys. Medd.*, 1926, **7**, No. 9.
[8] E. A. Guggenheim, *Trans. Faraday Soc.*, 1960, **56**, 1159.

1375. *Crystallographic Data for 2,2-Diphenyl-1-picrylhydrazyl*

By DONALD E. WILLIAMS

THE stable free radical 2,2-diphenyl-1-picrylhydrazyl crystallises in at least three solvent-free forms,[1] in addition to crystal forms containing solvent molecules. Preliminary measurements of lattice constants and space-group symmetries of diphenylpicrylhydrazyl-I and -III, as prepared by Weil and Anderson,[1] are now reported.

[1] J. A. Weil and J. K. Anderson, *J.*, 1965, 5567.

Diphenylpicrylhydrazyl-I.—This was obtained by crystallisation from ether solution. Weissenberg and precession X-ray diffraction photographs of single crystals showed orthorhombic symmetry. In the (0*kl*) zone reflections having ($k + l$) odd were absent, and in the (*h0l*) zone reflections having h odd were absent. The possible space groups are therefore *Pnam* if a centre of symmetry is present, or *Pna2₁* if a symmetry centre is absent.

The lattice constants were determined by a least-squares fit [2] to nine reflection angles which were carefully measured with a single-crystal diffractometer equipped with a scintillation-counter detector, using copper K_α radiation ($\lambda = 1.5418$ Å). Table 1 shows the

TABLE 1

Observed and calculated Bragg angles for diphenylpicrylhydrazyl-I

Miller indices ...	(020)	(031)	(120)	(0,0,14)	(2,0,13)	(006)	(201)	(601)	(602)
2θ (obs.)	22·68	34·50	23·30	47·40	45·23	19·84	11·08	32·24	32·75
2θ (calc.)	22·69	34·49	23·31	47·41	45·22	19·84	11·07	32·24	32·76

observed and calculated Bragg angles for the lattice constants $a = 16.75 \pm 0.01$, $b = 7.838 \pm 0.005$, and $c = 26.85 \pm 0.01$ Å. The crystals were thin needles elongated along b. The observed reflection widths were normal, but the small size of the crystal prevented angular measurements in the back-reflection region. The unit-cell volume is 3525·04 Å^3 and the calculated density for eight molecules in the unit cell is 1·485 g. cm.$^{-3}$.

Diphenylpicrylhydrazyl-III.—This was obtained by recrystallisation from carbon disulphide solution. Weissenberg and precession X-ray diffraction photographs of single crystals showed triclinic symmetry. The possible space groups are therefore $P\bar{1}$ if a centre of symmetry is present, or $P1$ if a centre of symmetry is absent.

The lattice constants were determined in the same way as for diphenylpicrylhydrazyl-I by a least-squares fit to 13 reflection angles. Table 2 shows the observed and calculated

TABLE 2

Observed and calculated Bragg angles for diphenylpicrylhydrazyl-III

Miller indices...	(002)	(070)	(5̄02)	(05̄2)	(23̄0)	(7̄20)	(0,13,0)	(414)	(2̄25)	(3̄,10,3)	(9̄21)	(1̄3̄5)	(9̄3̄1)
2θ (obs.)	24·05	33·33	37·49	33·00	18·50	48·15	64·41	63·10	62·74	63·24	61·60	62·90	67·60
2θ (calc.)	24·09	33·34	37·50	32·99	18·52	48·14	64·39	63·12	62·69	63·24	61·63	62·90	67·56

angles for the lattice constants $a = 13.58 \pm 0.01$, $b = 18.91 \pm 0.01$, $c = 7.555 \pm 0.005$ Å, $\alpha = 92.2 \pm 0.1$, $\beta = 101.6 \pm 0.1$, and $\gamma = 95.0 \pm 0.1$ deg. The observed cell constants were checked with the computer program of Lawton and Jacobson [3] to verify that the correct reduced triclinic cell was chosen and that no higher symmetry was present. The crystals showed an unusually large reflection width and a high temperature factor. Even though good sized crystals could be obtained, no X-ray reflections were observed in the back-reflection region. The needles are elongated along c, with faces (001), (100), (010), and (1̄10) well developed. The volume of the unit cell is 1890·14 Å^3 and the calculated density for four molecules in the unit cell is 1·385 g. cm.$^{-3}$.

Inokuchi, Harada, and Maruyama [4] reported a solvent-free orthorhombic form of diphenylpicrylhydrazyl, which crystallised from carbon disulphide solution, with the lattice constants $a = 17.6$, $b = 18.9$, and $c = 7.59$ Å. The lengths of their observed b and c cell edges are remarkably similar to the triclinic cell we observe. The volume of their unit cell is about one-third larger than the triclinic cell we report.

We wish to thank J. A. Weil and J. K. Anderson for kindly supplying us with crystals of diphenylpicrylhydrazyl-I and -III.

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AMES, IOWA, U.S.A.   [*Received, June 4th,* 1965.]

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[3] S. L. Lawton and R. A. Jacobson, AEC Report IS-1141, " The Reduced Cell and its Crystallographic Applications " (1965).

[4] H. Inokuchi, Y. Harada, and Y. Maruyama, *Bull. Chem. Soc. Japan*, 1962, **35**, 1559.