

Lyman R. Caswell*, Patricia Palacios, Suzanne J. Schmidt, Roya Anvar and Anabel Garcia

Department of Chemistry, The Texas Woman's University, Denton, Texas 76204

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Condensation of two equivalents of an aromatic cyclic anhydride with an aromatic diamine, or of two equivalents of an aromatic amine with an aromatic bisanhydride, results in the formation of an aromatic bisimide. Thirty-one such bisimides were prepared. The bisimides in which the two imide groups are connected by a fully coplanar system show extremely low solubilities and high melting and decomposition temperatures. Many are also strongly colored. It is suggested that these properties may result from intermolecular charge-transfer effects in the solid state, giving charge-transfer polymers.

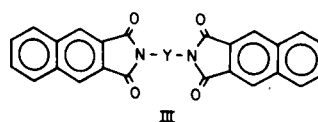
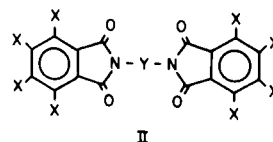
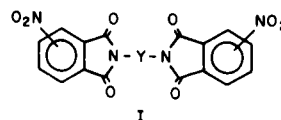
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Condensation of two equivalents of 3-nitrophthalic anhydride with *p*-phenylenediamine in nitrobenzene at 180°, according to the phthaloylation method of Caswell and Atkinson (2), resulted in the precipitation of 1,4-bis-(3-nitrophthalimido)benzene (I, 3-NO₂, Y = 1,4-C₆H₄). This was the expected product; but the physical properties it displayed were quite unanticipated. The material was insoluble in all common organic solvents. Purification for microanalysis was accomplished by extracting the impurities with boiling *N,N*-dimethylformamide. Attempts to measure the melting point by conventional methods showed no evidence for either melting or decomposition below 350°. The most striking physical property was the olive-green color of the pure compound. The isomeric 1,4-bis(4-nitrophthalimido)benzene (I, 4-NO₂, Y = 1,4-C₆H₄) showed similar properties, except that it was a lighter color, yellow green.

The original purpose for which these compounds had been prepared was to reduce them to novel diamines. Efforts to carry out these reductions by either standard catalytic or chemical techniques resulted in no reaction,

and the starting material was quantitatively recovered. The unusual failure of these nitro compounds to undergo reduction is probably a result of their extremely low solubilities.

A search of the literature was undertaken to determine if bisimides with similar properties had previously been reported. In 1942 Wanag (3) described a number of bis-(phthalimido)arenes, some of which had quite high melting points and low solubilities. Only two were also strongly colored. These were the yellow 4,4'-bis(phthalimido)stilbene, which melted at 428°, and the brown-yellow 1,5-bis(phthalimido)naphthalene, which melted with decomposition at 442-444°. A number of examples of bis(nitrophthalimides) (I) were found in the patent literature (4), but none of the disclosures indicated that these examples possess unusual physical properties. Patent disclosures of bis(tetrahalophthalimide)s (II) (5) and of *N,N'*-diaryl-1,8; 4,5-naphthalenebisimides (VI) (6) also indicated no unusual physical properties for these compounds. A pharmacological study (7) of some *N,N'*-bis(4-dialkylaminophenyl) derivatives of pyromellitimide (V) and of 1,8;4,5-naphthalene-



bisimide was likewise lacking in physical information. On the other hand, the strong colors and high melting points of the *N,N'*-diaryl-3,6-bis(arylamino)pyromellitimides are well documented (8), but these compounds differ from our examples in that they have the electron-donating amino groups in conjugation with the imide carbonyls, and their solubilities appear to be somewhat greater. A number of *N,N'*-diaryl-3,4;9,10-perylenebisimides are in use as dye-stuffs (9), but this is also not a comparable case, since the parent unsubstituted bisimide is also strongly colored. A study by Chlystek (10) in 1966, which was published in part in 1972, showed that *N,N'*-diarylpyromellitimides (V) have color (10a) and melting characteristics similar to those which we observed for the 1,4-bis(nitrophthalimido)benzenes. Wanag's and Chlystek's studies thus appear to be the only ones which are relevant. These studies are, however, limited to single structural classes of bisimides, and offer no explanations for the observed phenomena.

We have therefore prepared and examined a more diverse group of 31 aromatic bisimides. Table I provides data for 26 bis(phthalimide)s, of which 23 are bis(nitrophthalimide)s (I). Table II lists five *N,N'*-diaryl bisimides, including two of Chlystek's most colorful examples (Compounds 27 and 31), representative examples of 1,8;4,5-naphthalenebisimides (IV), and one 3,4;3,4'-benzophenonebisimide (VI).

Table I
Bis(phthalimido)arenes

Compound	Class	Structure	Yield %	Dec. Point °C	M.p., °C	Color	Elementary Composition	%C		%H		%N	
								Calcd.	Found	Calcd.	Found	Calcd.	Found
1	I, 3-NO ₂	4-C ₆ H ₄ SSC ₆ H ₄ -4	30	215	219	Yellow Green	C ₂₈ H ₁₄ N ₄ O ₈ S ₂	56.18	56.08	2.36	2.38	9.36	9.21
2	I, 4-NO ₂	4-C ₆ H ₄ SSC ₆ H ₄ -4	59	227	227	Brownish Yellow	C ₂₈ H ₁₄ N ₄ O ₈ S ₂	56.18	56.20	2.36	2.40	9.36	9.38
3	I, 3-NO ₂	4-C ₆ H ₄ CH ₂ C ₆ H ₄ -4	86	262	266 (a)	Greenish White (b)	C ₂₉ H ₁₆ N ₄ O ₈	63.51	63.54	2.94	2.98	10.22	10.27
4	I, 3-NO ₂	4-C ₆ H ₄ SC ₆ H ₄ -4	57	289	296	Orange Brown	C ₂₈ H ₁₄ N ₄ O ₈ S	59.37	59.31	2.49	2.52	9.89	9.93
5	I, 3-NO ₂	4-C ₆ H ₄ OC ₆ H ₄ -4	69	239	304 (c)	Yellow (d)	C ₂₈ H ₁₄ N ₄ O ₉	61.10	61.31	2.56	2.65	10.18	10.27
6	I, 4-NO ₂	4-C ₆ H ₄ ClI ₂ C ₆ H ₄ -4	60	303	305	Ivory	C ₂₉ H ₁₆ N ₄ O ₈	63.51	63.58	2.94	2.96	10.22	10.31
7	I, 4-NO ₂	4-C ₆ H ₄ SO ₂ C ₆ H ₄ -4	80	305	305	Cream	C ₂₈ H ₁₄ N ₄ O ₁₀ S	56.19	55.99	2.36	2.36	9.36	9.41
8	I, 4-NO ₂	4-C ₆ H ₄ OC ₆ H ₄ -4	67	--	320	Orange Yellow (e)	C ₂₈ H ₁₄ N ₄ O ₉	61.10	61.04	2.56	2.65	10.18	10.23
9	I, 4-NO ₂	4-C ₆ H ₄ SC ₆ H ₄ -4	47	--	325	Violet Brown	C ₂₈ H ₁₄ N ₄ O ₈ S	59.37	59.38	2.49	2.55	9.89	9.86
10	I, 3-NO ₂	1,3-C ₆ H ₄	72	332	342	Pale Yellow	C ₂₂ H ₁₀ N ₄ O ₈	57.65	57.53	2.20	2.27	12.22	12.31
11	I, 3-NO ₂	4-C ₆ H ₄ SO ₂ C ₆ H ₄ -4	17	342	--	Oyster White (f)	C ₂₈ H ₁₄ N ₄ O ₁₀ S	56.19	56.17	2.36	2.40	9.36	9.28
12	I, 3-NO ₂	4-C ₆ H ₄ N ₂ NC ₆ H ₄ -4	74	356	--	Olive Sepia	C ₂₈ H ₁₄ N ₆ O ₈	59.79	59.71	2.51	2.57	14.94	14.98
13	I, 4-NO ₂	1,3-C ₆ H ₄	74	--	357	Greenish Yellow	C ₂₂ H ₁₀ N ₄ O ₈	57.65	57.77	2.20	2.25	12.22	12.30
14	I, 4-NO ₂	4-C ₆ H ₄ CH ₂ CHC ₆ H ₄ -4	64	362	--	Orange Brown	C ₃₀ H ₁₆ N ₄ O ₈	64.29	64.49	2.88	2.99	10.00	9.86
15	I, 4-NO ₂	4-C ₆ H ₄ N ₂ NC ₆ H ₄ -4	60	386	--	Olive Brown	C ₂₈ H ₁₄ N ₆ O ₈	59.79	59.86	2.51	2.52	14.94	14.86
16	I, 3-NO ₂	4-C ₆ H ₄ CH ₂ CHC ₆ H ₄ -4	57	390	--	Orange Yellow	C ₃₀ H ₁₆ N ₄ O ₈	64.29	64.27	2.88	2.91	10.00	10.00
17	I, 4-NO ₂	4-C ₆ H ₄ C ₆ H ₄ -4	62	391	--	Orange Yellow	C ₂₈ H ₁₄ N ₄ O ₈	62.93	62.85	2.64	2.69	10.48	10.44
18	I, 3-NO ₂	1,5-naphthalene	58	414	--	Yellow	C ₂₆ H ₁₂ N ₄ O ₈	61.42	61.37	2.38	2.39	11.02	11.06
19	I, 4-NO ₂	1,4-C ₆ H ₄	78-86	415	--	Yellow Green	C ₂₂ H ₁₀ N ₄ O ₈	57.65	57.63	2.20	2.37	12.22	12.27
20	I, 3-NO ₂	4-C ₆ H ₄ C ₆ H ₄ -4	69	416	--	Greenish Yellow	C ₂₈ H ₁₄ N ₄ O ₈	62.93	62.87	2.64	2.79	10.48	10.48
21	I, 4-NO ₂	2,6-anthraquinone	84	421	--	Olive Gray	C ₃₀ H ₁₂ N ₄ O ₁₀	61.23	61.12	2.06	2.16	9.52	9.55
22	I, 4-NO ₂	1,5-naphthalene	60	430	--	Gray	C ₂₆ H ₁₂ N ₄ O ₈	61.42	61.52	2.38	2.43	11.02	11.09
23	III	1,4-C ₆ H ₄	92	480	480	Slate Purple	C ₃₀ H ₁₆ N ₂ O ₄	76.92	76.66	3.44	3.49	5.98	6.04
24	I, 3-NO ₂	1,4-C ₆ H ₄	77-89	(g)	--	Olive Green	C ₂₂ H ₁₀ N ₄ O ₈	57.64	57.74	2.20	2.24	12.22	12.27
25	II, X = Br	1,4-C ₆ H ₄	93	(h)	--	Grayish White	C ₂₂ H ₄ Br ₂ N ₂ O ₄	(i)	--	--	--	2.81	2.88
26	II, X = Cl	1,4-C ₆ H ₄	96	(h)	--	White	C ₂₂ H ₄ Cl ₂ N ₂ O ₄	(j)	--	--	--	4.36	4.36

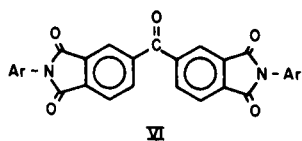
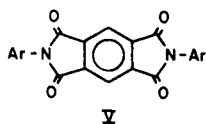
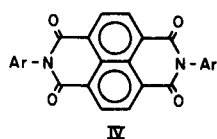
(a) Reported (3a) m.p., 268-270° (dec.). (b) Reported (3a) color, yellow. (c) Reported (3a) m.p., 303-304°. (d) Reported (3a) color, gold. (e) Reported (3a) color, orange. (f) Reported (3a) color, yellow. (g) No thermal transition below 500°. Gradual browning occurs on prolonged heating above 410°. (h) No thermal transition below 500°; however, the samples recrystallized into glittering metallic gray scales during heating to this temperature. (i) Percent Br, Calcd: 64.10. Found: 63.78. (j) Percent Cl, Calcd: 44.18. Found: 43.87.

Table II

N,N'-Diarylarenebisimides

Compounds	Class	Structure	Yield, %	Dec. Point,	M.p., °C	Color	Elementary Composition	%C		%H		%N	
								Calcd.	Found	Calcd.	Found	Calcd.	Found
27	V	4-C ₆ H ₄ N(CH ₃) ₂	80	382	(a)	Copper-bronze (b)	C ₂₆ H ₂₂ N ₄ O ₄	68.71	68.60	4.88	4.91	12.33	12.41
28	VI	4-C ₆ H ₄ N(CH ₃) ₂	82	391	391	Yellow	C ₃₃ H ₂₆ N ₄ O ₅	70.96	70.98	4.98	4.70	10.03	10.08
29	IV	4-C ₆ H ₄ N(CH ₃) ₂	73	410	406 (c)	Plum	C ₃₀ H ₂₄ N ₄ O ₄	71.42	71.22	4.80	4.82	11.10	11.07
30	IV	4-C ₆ H ₄ OCH ₃	86	431	431	Olive Yellow	C ₂₈ H ₁₈ N ₂ O ₆	70.29	70.05	3.79	3.82	5.85	5.77
31	V	4-C ₆ H ₄ OCH ₃	52	445 (d)	445	Deep Bright Yellow(e)	C ₂₄ H ₁₆ N ₂ O ₆	67.29	67.34	3.76	3.77	6.54	6.57

(a) Reported m.p., 348-358° (8), 370-376° (6). (b) Reported (8a) color, copper-bronze. (c) Reported (6) m.p., 363-364°. (d) Reported (8) decomposition with sublimation at 400-428°. (e) Reported (8a) color, deep yellow.



Examination of these compounds with a differential scanning calorimeter permitted measurement of melting points. Visual inspection of the samples after the melting points had been determined showed whether melting had been accompanied by decomposition. The majority of the bis(nitrophthalimide)s showed an exotherm, either a few degrees below the melting endotherm, or instead of the melting endotherm. These exotherms were always accompanied by irreversible discoloration of the sample (browning or blackening) without melting, and were therefore interpreted as decompositions. The entries in the tables are arranged in order of increasing decomposition point or melting point.

The majority of the compounds were fine powders. The colors of these powders were dull in appearance, resembling tones of earth, desert, or dead vegetation. Collectively they can be described as "camouflage colors." There were two spectacular exceptions, *N,N'*-bis(4-dimethylaminophenyl)pyromellitimide (Compound **27**, V, Ar = 4-C₆H₄N(CH₃)₂) and *N,N'*-bis(4-dimethylaminophenyl)-1,8,4,5-naphthalenebisimide (Compound **29**, IV, Ar = 4-C₆H₄N(CH₃)₂). Both of these compounds crystallized from the reaction mixtures as beautifully colored, glittering metallic scales. The two bis(tetrahalophthalimido)benzenes (Compounds **25** and **26**, II, X = Br or Cl) recrystallized into similarly lustrous scales on heating to 500°, without passing through a detectable thermal transition.

Unusually high melting points and low solubilities of organic compounds can often be associated with strong intermolecular hydrogen-bonding. This effect is not possible with any of the compounds in the present study. Strong colors in aromatic compounds are often attributable either to the bathochromic effects of an extended polycyclic conjugated system, as in the case of the *N,N'*-diaryl-3,4,9,10-perylenebisimides (9), or to the favoring of quinonoid structures through electron donation across a ring

from a donor group to an acceptor group, as in the cases of the aminophthalimides (2a, 11) and the diaminopyromellitimides (8). These effects also cannot occur with the compounds of the present study.

The properties of the compounds in Table II, and of Compounds **12** and **14-26** in Table I, can be explained as the results of intermolecular charge-transfer effects between molecules in parallel planes in the crystal structures of these compounds (12a). The bisanhydrides from which structures II, IV and V are derived are already well known as charge-transfer acceptor molecules (12b). The imide group, like the anhydride group, strongly withdraws electrons by both resonance and induction from the aromatic ring to which the two carbonyl groups of the imide are bonded (1), but resonance donation of electrons cannot occur from the *N*-substituent. In the naphthalenebisimides (IV) and pyromellitimides (V), we thus have structures in which the central aromatic rings are electron deficient, while the *N*-substituents are electron-rich but unable to donate electrons within the molecule. Charge must then be balanced by charge transfer from donor *N*-substituents in one molecule to acceptor aromatic imide moieties in adjacent molecules. The simplest model for these effects would have the molecular planes parallel, with acceptor groups lying above or below donor groups. Since each molecule contains both donor and acceptor groups, the result is a refractory charge-transfer polymer. The arrangement is probably similar with the benzophenonebisimides VI, though complicated by the presence of the carbonyl group in the middle of the molecule. Either *n*-donation or *π*-donation is possible with the examples in Table II. We prefer *π*-donation to explain these charge-transfer effects because *n*-donation is not possible for a number of the *N,N'*-diarylpyromellitimides described by Chlystek. In the bis(phthalimide)s in Wanag's study (3) and in Table I, the acceptor groups are the phthalimide groups at the ends of the molecules, and the donors are the aromatic groups bonded to the two imide nitrogens. In these cases only *π*-donation is possible.

Comparatively low melting points and moderate to high solubilities in DMF are displayed by Compounds **1-9** and **11** in Table I, and by the analogous bis(phthalimide)s described by Wanag. All of these compounds have central groups whose bond angles are such that the two halves of the molecule cannot be coplanar with each other. In these cases the molecules cannot be stacked in the crystal structure in parallel planes, and the opportunities for intermolecular charge transfer are not as good. Compound **10**, 1,3-bis(3-nitrophthalimido)benzene, appears to be an intermediate case which does not fit well into either group of compounds. It is possible that this molecule may be slightly distorted from full coplanarity by steric effects.

Charge-transfer complexes are often strongly colored. This property cannot in itself be taken as evidence for

charge transfer in the absence of other indications. With the compounds which we have identified as charge-transfer complexes in this study, strong color is observed where functional groups provide dipoles which are at angles to the long axis of the molecule. The nitro groups of the bis(nitrophthalimide)s **12**, **14-22** and **24** provide such dipoles. The group dipoles of the methoxy and dimethylamino groups at the ends of the molecules listed in Table II may also be oriented at angles to the molecular plane. These observations provide an interesting speculation, as to whether the compounds in question might possess two differently colored crystal forms, depending on whether the molecules are laid down in the crystal with their group dipoles in a *cis* geometry, giving a net molecular dipole moment, or in a *trans* geometry, resulting in nonpolar molecules. That the color is a function of the crystal structure rather than the molecular structure is indicated by the fact that those compounds which did display some solubility in DMF or alcohol failed to give colored solutions. This effect of solvents was also observed with some of the compounds studied by Chlystek.

Wanag's bis(phthalimide)s (**3**) show that strong color is absent in the absence of group moments at angles to the molecular axis. The lack of color in the 1,4-bis(tetrahalophthalimido)benzenes (**25** and **26**) suggests that color may be lost when the group dipoles cancel each other to give net molecular moment of zero. The least strongly colored of Chlystek's compounds (**10a**) were those in which the two group dipoles cancelled each other, as, for example, in the light-yellow compounds *N,N'*-diphenylpyromellitimide (*V*, Ar = C₆H₅), *N,N'*-bis(4-tolyl)pyromellitimide (*V*, Ar = 4-CH₃C₆H₄), and *N,N'*-bis(4-nitrophenyl)pyromellitimide (*V*, Ar = 4-O₂NC₆H₄). These observations suggest that the polar *cis* orientation of the group dipoles is the geometry of the molecules as they are laid down in the structures of the colored crystals.

It has been reported (**13**) that the infrared absorption bands, characteristic of the functional groups involved in charge transfer, will be slightly shifted in comparison with the bands of the same groups in the uncomplexed substances. We determined the infrared absorption spectra of all of the nitro compounds in this study, using KBr pellets. The spectra were compared with the corresponding nitrophthalimides and *N*-phenylnitrophthalimides, none of which show any charge-transfer characteristics. The small differences in carbonyl, nitro and ring frequencies which were observed were as easy to interpret on the basis of substituent differences as on the basis of charge-transfer. The two effects are of the same order of magnitude. Conclusive spectrometric evidence for charge transfer in these compounds would require comparing the spectra of the solids with the spectra of solutions for the same compounds.

Two of the compounds, the olive-green 1,4-bis(3-nitrophthalimido)benzene (**24**) and the yellow-green 1,4-bis(4-

nitrophthalimido)benzene (**19**), were tested as pigments by a commercial laboratory (**14**). Compound **24** was rated as poor in respect to both heat resistance and lightfastness, while **19** had fair heat resistance and good lightfastness. Both substances had poor tint value.

EXPERIMENTAL

Synthesis of Aromatic Bisimides.

In typical preparation, 0.025 mole of the phthalic anhydride and 0.0125 mole of an aromatic diamine, or 0.025 mole of an aromatic amine and 0.0125 mole of an aromatic bisanhydride, were heated together under reflux with magnetic stirring to 160-190° in 100 ml. of nitrobenzene. The reaction usually initiated, with vigorous bubbling, at 175-185°, followed by gradual decline of the temperature of the mixture to 160-165° as the reaction progresses. The heating was discontinued when sufficient precipitate had formed to stop the stirring, or at the end of one hour, whichever came first. The reaction mixture was then allowed to cool to room temperature and was filtered by suction. The precipitate was washed free of nitrobenzene with 95% ethanol. The product was then purified by extraction with 100 ml. of boiling 95% ethanol (Compounds **2, 3, 6, 7, 11, 12**, and **15**) or with 50 ml. of boiling DMF (Compounds **1, 4, 5, 8-10, 13, 14**, and **16-31**). In most cases, two such extractions were needed to obtain a product which gave a satisfactory microanalysis (**15**). The yields reported in Tables I and II are the yields of these purified materials. Low yields thus indicate unusually soluble compounds rather than inefficient syntheses.

The *o*-dicarboxylic acids could be used in these syntheses in place of their anhydrides, with no diminution of yield, in agreement with earlier findings (**2**). Compounds **14, 16, 17**, and **20** were synthesized from the diamine dihydrochlorides instead of the free diamines.

The method of imide synthesis used here failed to give satisfactory results when the diamine was *o*-phenylenediamine, 1,4-diaminoanthraquinone, or 1,5-diaminoanthraquinone, or when the bisanhydride was 3,4,9,10-perylenetetracarboxylic bisanhydride. Attempts to prepare trisimides from mellitic anhydride or from melamine were also unsuccessful.

Measurement of Physical Properties.

Decomposition and melting temperatures were measured with the assistance of a Perkin-Elmer DSC-1B differential scanning calorimeter. After completion of each measurement the cooled capsule was opened and the contents were inspected for visible changes. Visual observations of these changes below 350° were made with an Electrothermal melting point apparatus. The colors of the compounds were in most cases identified with the assistance of a Stanley Gibbons Stamp Colour Key (**16**). Infrared absorption spectra were measured with a Perkin-Elmer 225 infrared spectrophotometer.

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REFERENCES

- (1) Previous paper in this series: L. R. Caswell, L. Y. Soo, D. H. Lee, R. G. Fowler, and J.-A. B. Campbell, *J. Org. Chem.*, **39**, 1527 (1974).

- (2a) L. R. Caswell and P. C. Atkinson, *ibid.*, **29**, 3151 (1964);
(b) L. R. Caswell and P. C. Atkinson, *J. Heterocyclic Chem.*, **3**, 328 (1966); (c) L. R. Caswell and E. D. Martínez, *J. Chem. Eng. Data*, **13**, 286 (1968).
- (3) G. Wanag, *Chem. Ber.* **75B**, 719 (1942).
- (4a) General Electric Co., German Offen. 2,261,714, 20 June 1974; (b) French Demande 2,210,609, 12 July 1974; (c) German Offen. 2,429,575; 16 Jan. 1975
- (5a) Raychem Corp., German Offen. 1,946,924; 4 Feb. 1971; (b) Siemens A.-G., German Offen. 1,951,632; 6 May 1971
- (6a) Farbenfabriken Bayer A.-G., Belgian Patent 651,245; 1 Feb. 1965; (b) Netherlands Appl. 6,408,816; 3 Feb. 1965; *Chem. Abstr.* **63**, 1755h (1965).
- (7) N. V. Khromov-Borisov, M. L. Indenbom and A. F. Danilov, *Khim.-Farm. Zh.*, **5**, 3 (1971).
- (8a) H. Hopff and B. K. Manukian, *Helv. Chim. Acta.*, **43**, 1645 (1960); *ibid.*, **44**, 700 (1961); *ibid.*, **45**, 1287, 1799 (1962); (b) B. K. Manukian, *ibid.*, **44**, 1922 (1961); *ibid.*, **46**, 2747 (1963).
- (9a) M. O. Shrader, U. S. Patent 1,543,747; 6 March 1951; *Chem. Abstr.*, **45**, 5940e (1951); (b) T. Maki and A. Hashimoto, *J. Chem. Soc. Japan, Ind. Chem. Sect.* **54**, 544 (1951); *Chem. Abstr.*, **47**, 6143b (1953).
- (10a) S. J. Chlystek, Ph.D. Dissertation, University of Delaware, 1966; (b) W. M. Mosher and S. J. Chlystek, *J. Heterocyclic Chem.*, **9**, 319 (1972).
- (11) A. Arcoria and F. Bottino, *Ann. Chim. (Rome)*, **51**, 411 (1961).
- (12a) R. Foster, "Organic Charge-Transfer Complexes", Academic Press, London, 1969, Chapter 8; (b) *ibid.*, Chapter 1.
- (13) M. A. Slifkin, *Spectrochim. Acta*, **29A**, 835 (1973).
- (14) Chemetron Corporation, Pigments Division, Holland, Michigan.
- (15) Atlantic Microlab Inc., Atlanta, Georgia.
- (16) Stanley Gibbons Ltd., London, England.