Nonclassical Heterocycles. 6. Tri- and Tetracyclic Ring Systems Containing a "Nonclassical" Thiophene Nucleus

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The in situ generation of azomethine imine ylides from 1-aminopyridinium, 1-aminoquinolinium, and 2-aminoisoquinolinium salts and their subsequent cycloaddition to dibenzoylacetylene has been utilized as a route to a series of 2,3-dibenzoylpyrazolo[1,5-*a*]pyridines, to 2,3-dibenzoylpyrazolo[1,5-*a*]quinoline, and to 1,2-dibenzoylpyrazolo[5,1-*a*]isoquinoline, respectively. Treatment of these dibenzoyl heterocycles with P_4S_{10}/pyridine readily gave several new "nonclassical" thiophene ring systems, the thieno[3,4-*b*]pyrazolo[1,5-*a*]pyridine-2-S^{IV} system containing 14π electrons and the thieno[3′,4′:3,4]pyrazolo[1,5-*a*]quinoline-2-S^{IV} and the thieno[3′,4′:3,4][5,1-*a*]isoquinoline-2-S^{IV} systems each containing 18π electrons. The diketones also reacted readily with hydrazine forming the corresponding ring-fused pyridazines. Cycloaddition with fumaronitrile and *N*-phenylmaleimide occurred exclusively across the thiocarbonyl ylide dipole of these "nonclassical" thiophene ring systems, H_2S being eliminated from the initial 1:1 cycloadducts under the thermal reaction conditions. However, dimethyl acetylenedicarboxylate and dibenzoylacetylene only underwent cycloaddition with those ring systems containing the quinoline and isoquinoline systems, sulfur being extruded readily from the initial 1:1 cycloadduct. 8,9-Dibenzoyl-7,10-diphenylbenzo[*b*]pyrazolo[1,5-*a*]quinoline prepared in this way was also converted with P_4S_{10}/pyridine into the thieno[3′,4′:8,9]benzo[*b*]pyrazolo[1,5-*a*]quinoline-9-S^{IV} ring system, a stable tetravalent sulfur system containing 22π electrons in which cycloaddition also occurred across the thiocarbonyl ylide dipole. With dimethyl acetylenedicarboxylate, sulfur was extruded from the initial 1:1 cycloadduct, whereas with fumaronitrile, the initial 1:1 cycloadduct itself was isolated. Incorporation of a tetravalent sulfur atom into a heterocyclic system and cycloaddition with olefinic or acetylenic dipolarophiles provide a convenient means of annulation of a benzene ring containing a variety of functional groups to the heterocyclic system.

Bicyclic 10π-electron heterocycles containing a "nonclassical" thiophene nucleus form a group of compounds of considerable theoretical interest and potential practical utility.[2] Eight of nine possible bicyclic heterocyclic ring systems have now been synthesized,[3] and of these, the thieno[3,4-*c*]pyrazole system **1** showed considerable promise for further development. Its stability was relatively unaffected by the nature of the substituents in the pyrazole ring, and although it reacted readily with oxygen in solution, in the solid state it was quite stable, particularly in the absence of light. Reaction with acetylenic and olefinic dipolarophiles occurred[4] exclusively at the thiocarbonyl ylide dipole to give indazoles **2** by thermal elimination of S or H_2S, respectively, from the initial 1:1 cycloadducts. This provides an excellent method of annulation of a benzene ring to a heterocyclic system, and in this publication we have extended these concepts to more complex heterocycles which contain, as partial structures, the thieno[3,4-*c*]pyrazole ring system.

Numerous possibilities exist for formation of ring-fused pyrazoles by initial amination of a trigonal nitrogen atom in a heterocyclic ring system followed by cycloaddition[5] onto the adjacent carbon atom. This publication describes results obtained with the pyridine, quinoline, and isoquinoline ring systems, having reported in an earlier publication[6] those in the thiazole series where isomeric products were obtained.

1,3-Diphenylthieno[3,4-*b*]pyrazolo[1,5-*a*]pyridines-2-S^{IV} (8). Pyridine and its 2- and 4-methyl derivatives were readily aminated[7] with hydroxylamine-*O*-sulfonic acid,[8] and the resultant salts, in addition to their iodides, were also characterized as their picrates.[9] When a solution of these salts **3** in DMF was treated with K_2CO_3 at room temperature, the reaction mixture rapidly developed a deep blue-green color attributed to the formation of the azomethine imines **4** which were trapped with dibenzoylacetylene to form a postulated 1:1 cycloadduct **5**. This adduct underwent ready aerial oxidation under reaction workup conditions, and the 2,3-dibenzoylpyrazolo[1,5-*a*]pyridines **6** were obtained in good yields. Azomethine imines of type **4** have been utilized previously in cycloadditions with activated dipolarophiles,[10] and on reaction with ethyl propiolate, the corresponding 3-ethoxycarbonyl derivative was formed.[11] The NMR data for **6a**, **6b**, and **6c** were in agreement with that of the ethyl propiolate product (Experimental Section) and provided confirmation of these structures. Carbonyl absorption bands typical of diaryl ketones were observed in the 1665–1620 cm^{-1} region, and all products were characterized by intense molecular ions, close correspondence of the observed intensities of the $[M + 1]^{+\cdot}$ and $[M + 2]^{+\cdot}$ ions with the calculated values, and doubly charged molecular ions. Other fragmentations were also consistent with these structures.

(1) Abstracted in part from the M.S. Theses of H.P.Y. and S.J.Z, Rensselaer Polytechnic Institute, Troy, N.Y., 1976.

(2) Reviews dealing with this topic include the following: Cava, M. P.; Lakshmikantham, M. V. *Acc. Chem. Res.* **1975**, *8*, 139. Potts, K. T. "Special Topics in Heterocyclic Chemistry"; Weissberger, A.; Taylor, E. C., Eds.; Wiley: New York, 1977; Chapter 6. Ramsden, C. A. *Tetrahedron* **1977**, *33*, 3203.

(3) Recent syntheses include the thieno[3,4-*c*]isothiazole system [Gotthardt, H.; Reiter, F. *Tetrahedron Lett.* **1976**, 2163], the thieno[3,4-*c*][1,2,5]oxadiazole system [Tsuge, O.; Takata, T.; Noguchi, M. *Heterocycles* **1977**, *6*, 1173], and the thieno[3,4-*c*][1,2,3]triazole system [Potts, K. T.; Considine, J., unpublished results].

(4) Potts, K. T.; McKeough, D., *J. Am. Chem. Soc.* **1974**, *96*, 4276.

(5) E.g., see Zugravescu, I.; Peterovanu, M. "N-Ylide Chemistry", McGraw-Hill: New York, 1976. Timpe, H. J., *Adv. Heterocycl. Chem.*, **1974**, *17*, 213.

(6) Potts, K. T.; Chaudhury, D. R. *J. Org. Chem.* **1977**, *42*, 1648. See also *J. Org. Chem.* **1976**, *41*, 187.

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(8) Matsuguma, H. J.; Audrieth, L. *Inorg. Synth.* **1957**, *5*, 122.

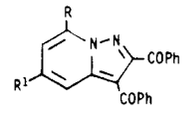
(9) Okamoto, T.; Hirobe, M.; Ohsawa, A. *Chem. Pharm. Bull. Jpn.* **1966**, *14*, 518.

(10) Huisgen, R.; Grashey, R.; Krischke, R. *Tetrahedron Lett.* **1962**, 387.

(11) Boekelheide, V.; Fedoruk, N. A. *J. Org. Chem.* **1968**, *33*, 2062.

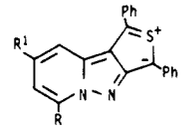
0022-3263/80/1945-0090$01.00/0

Table I



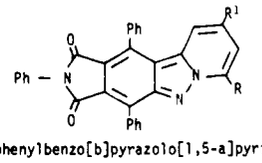
Some 2,3-Dibenzoylpyrazolo[1,5-a]pyridines (6)

R	R^1	Mp °C	Yield %	Formula[a]	M+ (rel int)	ν_{CO} (KBr) cm^{-1}	Spectral Data NMR δ ($CDCl_3$)	λmax (CH_3OH) nm (log ε)
H	H	141.5-142.5	56[b]	$C_{21}H_{14}N_2O_2$	326 (50)	1650, 1625	6.94-7.91 (m, 12, aromatic), 8.11 (dd, 1, C_4-H, J = 9.0 Hz), 8.63 (dd, 1, C_7-H, J = 7.0 Hz)	217 (4.57), 253 (4.43), 316 (4.10)
H	CH_3	122-124	28[c]	$C_{22}H_{16}N_2O_2$	340 (26)	1660, 1640, 1620	2.46 (s, 3, CH_3), 6.92 (dd, 1, C_6-H, J = 7.0 Hz), 7.02-8.02 (m, 11, aromatic), 8.51 (d, 1, C_7-H, J = 7.0 Hz).	223 (4.52), 254 (4.42), 322 (4.07)
CH_3	H	122-123.5	18[d]	$C_{22}H_{16}N_2O_2$	340 (33)	1660, 1640 1620	2.46 (s, 3, CH_3), 6.92 (dd, 1, C_6-H, J = 7.0 Hz), 7.02-8.02 (m, 11, aromatic), 8.51 (d, 1, C_7-H, J = 7.0 Hz).	223 (4.52), 254 (4.42), 322 (4.07)



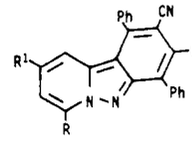
Some 1,3-Diphenylthieno[3,4-b]pyrazolo[1,5-a]pyridines-2-S^{IV} (8)

H	H	149.5-150.5	62[e]	$C_{21}H_{14}N_2S$	326 (100)	—	6.80-8.20 (m, 13, aromatic), 8.55 (dd, 1, C_6-H, J = 5.0 Hz)	221[h] (4.41), 256 (4.59), 264[h] (4.15), 326 (4.33), 424[h] (3.71), 481 (4.05)
H	CH_3	195-198	81[f]	$C_{22}H_{16}N_2S$	340 (95)	—	2.40 (s, 3, CH_3), 6.94 (dd, 1, C_7-H, J = 7.5 Hz), 7.11-8.23 (m, 11, aromatic), 8.57 (d, 1, C_6-H, J = 7.0 Hz).	221 (4.47), 259 (4.21), 274 (4.21), 327 (4.48), 402 (3.93), 488 (4.28)
CH_3	H	216-216.5	79[g]	$C_{22}H_{16}N_2S$	340 (92)	—	2.93 (s, 3, CH_3), 7.06-8.36 (m, 13, aromatic)	208 (4.30), 244 (4.11), 266[h] (3.95), 318 (4.18), 380 (3.39), 477 (3.84)



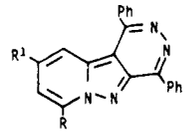
Some N,7,10-Triphenylbenzo[b]pyrazolo[1,5-a]pyridine-8,9-dicarboximides(10)

H	H	307-310 decomp	56[i]	$C_{31}H_{19}N_3O_2$	465 (100)	1760, 1710	6.90-8.04 (m, 18, aromatic), 8.85 (dd, 1, C_4-H, J = 6.0 Hz)[j]	276 (4.57), 365 (4.22)
H	CH_3	345-346.5	63[k]	$C_{32}H_{21}N_3O_2$	479 (100)	1750, 1700	2.51 (s, 3, CH_3), 6.90-7.87 (m, 17, aromatic), 8.80 (d, 1, C_4-H, J = 7.0 Hz)[j]	206 (4.25), 215[h] (4.14), 279 (4.36), 373 (4.04)
CH_3	H	348-350	42[l]	$C_{32}H_{21}N_3O_2$	479 (100)	1760, 1710	2.99 (s, 3, CH_3), 7.12-8.22 (m, 18, aromatic)[j]	273 (4.25), 367 (3.98)



2,3-Dicyano-1,4-diphenylbenzo[b]pyrazolo[1,5-a]pyridine (11)

H	H	330-333 decomp	44[m]	$C_{25}H_{14}N_4$	370 (100)	2210 (CN)	7.58-8.21 (m, 13, aromatic), 9.25 (dd, 1, C_7-H, J = 7.0 Hz)[j]	266 (4.65), 345 (4.19), 385 (3.91), 404 (3.88)



Some 1,4-Diphenylpyrido[1',2':2,3]pyrazolo[3,4-d]pyridazines (7)

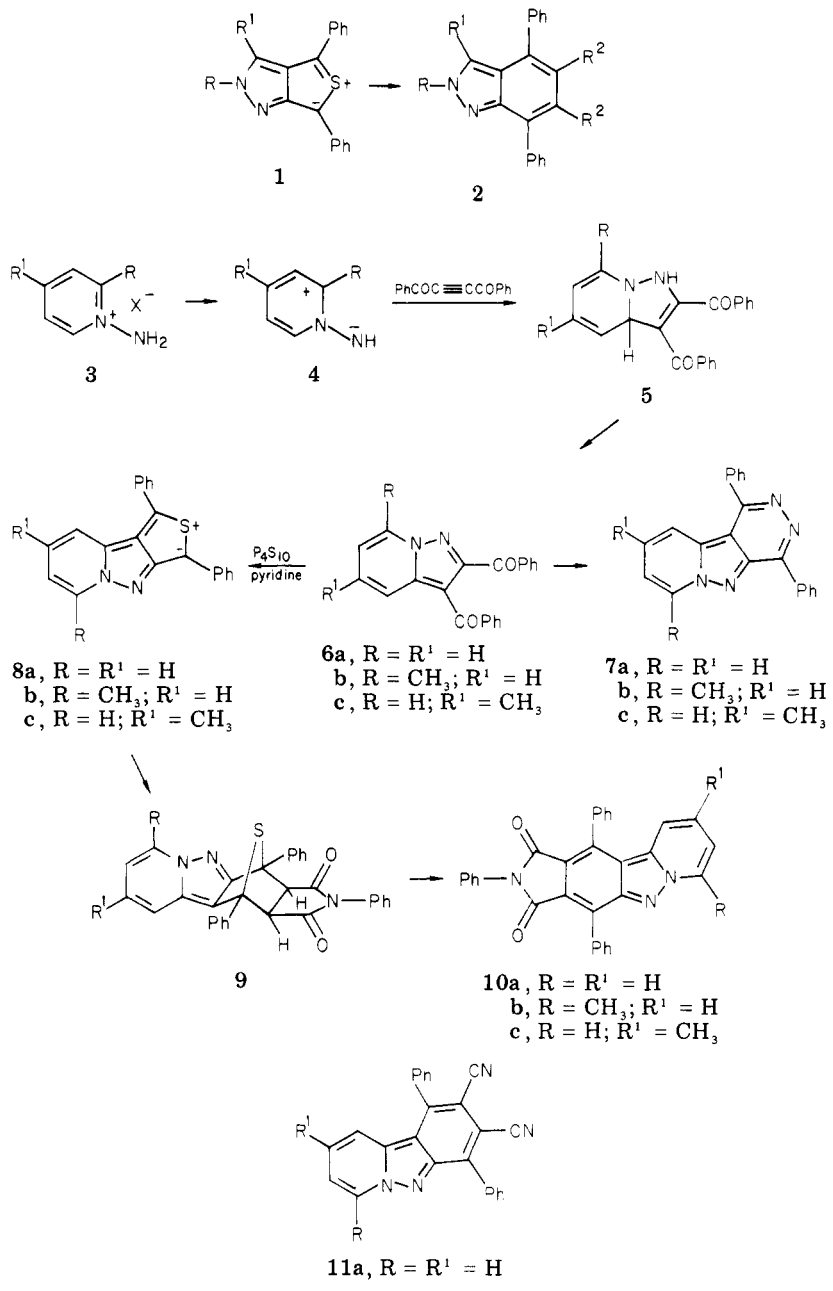
H	H	226-227 decomp	53[l]	$C_{21}H_{14}N_4$	322 (81)	—	7.34-8.67 (m, 13, aromatic), 9.27 (dd, 1 C_7-H, J = 7.0 Hz)[j]	231 (4.43), 268 (4.27), 283[h] (4.34), 316[h] (4.10), 368 (4.11)
H	CH_3	285-287	63[l]	$C_{22}H_{16}N_4$	336 (65)	—	2.72 (s, 3, CH_3), 7.50-8.78 (m, 12, aromatic), 9.27 (d, 1, C_7-H, J = 7.0 Hz)[j]	233[h] (4.30), 269 (4.32), 315[h] (4.04), 374 (4.04)
CH_3	H	265-268	81[l]	$C_{22}H_{16}N_4$	336 (68)	—	3.25 (s, 3, CH_3), 7.33-8.90 (m, 13, aromatic)[j]	212 (4.42), 233 (4.23), 245 (4.19), 270 (4.32), 284 (4.29), 315[h] (4.04), 360[h] (3.97), 376 (4.05)

[a] Satisfactory analytical data (± 0.4% for C, H, N) were reported for all new compounds listed in the Table. [b] Golden-yellow plates from isopropanol. [c] Cream plates from isopropanol. [d] Cream blades from EtOH. [e] Brick-red needles from EtOH. [f] Orange-red needles from aqueous EtOH. [g] Bright-red needles from aqueous EtOH. [h] Shoulder. [i] Lemon-yellow irregular prisms from dioxane. [j] CF_3CO_2D. [k] Yellow irregular prisms from dioxane. [l] Yellow needles from aqueous EtOH. [m] Pale yellow micro-needles from 1,2-dichloroethane.

Reaction of the dibenzoyl derivatives **6** with anhydrous hydrazine afforded the corresponding ring-fused pyridazines **7**. Thus **6a** gave 1,4-diphenylpyrido[1′,2′:2,3]-pyrazolo[3,4-*d*]pyridazine (**7a**) as yellow needles in 53% yield, providing a convenient characterization of these dibenzoyl derivatives.

Phosphorus pentasulfide treatment of **6** in refluxing pyridine, followed by quenching the reaction mixture in

Scheme I



ice water and subsequent recrystallization, gave a series of "nonclassical" thiophenes 8 described in Table I. Thus **6a** afforded 1,3-diphenylthieno[3,4-*b*]pyrazolo[1,5-*a*]-pyridine-2-S^{IV} (**8a**) as small, brick-red needles in 62% yield. The tetravalent sulfur systems 8 were sufficiently stable to be recrystallized from ethanol[12] and were relatively nonpolar, moving rapidly on TLC with benzene as the developing solvent, and their highly fluorescent $CHCl_3$ solutions were rapidly bleached on exposure to light and air.

In the mass spectra of 8, their molecular ions dominated the simple spectra with the intensity of the $[M + 1]^+$· ions in agreement with calculated values. The more important ions observed were the doubly charged molecular ions, the thiobenzoylium ion, m/e 121, and the phenyl ion, m/e 77. The fact that 8 did not fragment significantly by loss of a phenyl radical is consistent with the results obtained in the mass spectra of 2-phenylthiophene,[13] 2,5-diphenylthiophene,[13] and tetraphenylthiophene.[14]

Reaction of 8 with *N*-phenylmaleimide in refluxing xylene occurred readily with elimination of H_2S. From **8a**, *N*,7,10-triphenylbenzo[*b*]pyrazolo[1,5-*a*]pyridine-8,9-dicarboximide (**10a**) was isolated, no trace of the intermediate **9** being detected although TLC of the recrystallization mother liquors suggested the presence of a trace of some other product. Evidence in support of structure **10** is presented in Table I.

Similarly, fumaronitrile underwent ready reaction with 8 in refluxing xylene with immediate evolution of H_2S. After 11 h, reaction workup afforded 2,3-dicyano-1,4-diphenylbenzo[*b*]pyrazolo[1,5-*a*]pyridine (**11a**) as pale yellow microneedles in 44% yield, mp 330–333 °C dec. The yield of **11a** dropped to 15% when benzene was used as the solvent. Spectral data consistent with structure **11** are listed in Table I. Reaction between 8 and *trans*-1,2-dibenzoylethylene, norbornylene, ethyl vinyl ether, tetra-

(12) Cf. Cava, M. P.; Sprecker, M. A. *J. Org. Chem.* **1973**, *38*, 3975.
(13) Bowie, J. H.; Cooks, R. G.; Lamesson, S. O.; Nodle, C. *J. Chem. Soc. B* **1967**, 616.
(14) American Petroleum Research Project 44, Catalog of Mass Spectral Data, Spectrum 1408.

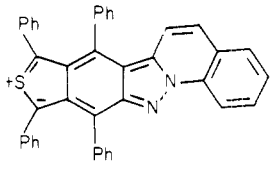
detected during this reaction, and the structure of **19** was readily established from the spectral data.

Both dimethyl acetylenedicarboxylate and dibenzoylacetylene underwent reaction with **16** in refluxing xylene, although extended reaction times were required for complete reaction to occur. The intermediate **20** (R = $COOCH_3$ and COPh, respectively) was undoubtedly involved in the reaction, the final products, dimethyl 7,10-diphenylbenzo[*b*]pyrazolo[1,5-*a*]quinoline-8,9-dicarboxylate (**19**, R = $COOCH_3$) (76%) and 8,9-dibenzoyl-7,10-diphenylbenzo[*b*]pyrazolo[1,5-*a*]quinoline (**19**, R = COPh) (38%), being formed by elimination of sulfur from the appropriately substituted intermediate **20**. Spectral characterization of these two secondary cycloadducts is described below.

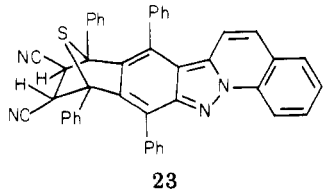
In the isoquinoline series it was not necessary to separate the mixture of 1,2-dibenzoylpyrazolo[5,1-*a*]isoquinoline (**15**) and its dihydro derivative **14** before reaction with P_4SO_{10}/pyridine. 1,3-Diphenylthieno[3′,4′:3,4]pyrazolo-[5,1-*a*]isoquinoline-2-S^{IV} (**21**) was obtained as brick-red, irregular prisms in poor yield. It was always contaminated with unreacted **15** under these reaction conditions, the **15** being readily removed by extraction with hot ethanol. The "nonclassical" thiophene **21** was quite stable in the solid phase, but in solution the deep-red color bleached rapidly. The poor yield of **21** obtained above may be attributed to the severe steric crowding between the 1-phenyl substituent and the benzene ring of the isoquinoline moiety.

7,8,10,11-Tetraphenylthieno[3′,4′:8,9]benzo[*b*]pyrazolo[1,5-*a*]quinoline-9-S^{IV} (22). 8,9-Dibenzoyl-7,10-diphenylbenzo[*b*]pyrazolo[1,5-*a*]quinoline (**19**, R = COPh) prepared above has two *vic*-benzoyl groups in the appropriate relationship for the formation of a thiophene ring. Accordingly, on treatment of **19** (R = COPh) with P_4S_{10} in refluxing pyridine, **22** was readily formed and isolated as navy-blue, irregular prisms, mp 260–262 °C (63%). This represents the first stable representative of a 22π-electron system containing "tetravalent" sulfur in a five-membered ring. Dilute solutions of **22** were rapidly bleached on exposure to light, probably by addition of oxygen to the thiocarbonyl ylide system.

Absorption maxima were observed in the ultraviolet spectrum of **22** at 390 and 310 nm and in the visible at 632



22



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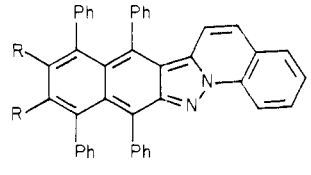

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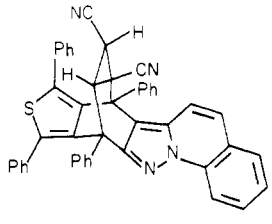


24

nm. The NMR spectrum consisted of two aromatic multiplets, δ 6.73–7.70 (21 protons) and δ 7.79–8.41 (4 protons), and an aromatic doublet, δ 8.67 (1 proton, J = 8.0 Hz). The most abundant ion in the mass spectrum corresponded to the molecular ion m/e 578 (100%), and the doubly charged molecular ion, m/e 289 (43%), was also evident.

Treatment of **22** with fumaronitrile in refluxing xylene resulted in the formation of a primary 1:1 cycloadduct, mp 282.5–284.5 °C, isolated as fawn irregular prisms. Two possible structures **23** and **24** were considered for this adduct as addition could occur across either the 8 and 10 positions or the 7 and 11 positions. The mass spectrum showed a low intensity molecular ion m/e 656, with the primary mode of fragmentation being a thermal retro-Diels–Alder reaction to the initial components of the reaction, both being detected in the spectrum. A less prominent mode of electron-impact fragmentation was initiated by loss of the sulfur bridge to give ion m/e 624. Further decomposition by two successive eliminations of hydrogen atoms gave ion m/e 622 which would correspond to **25** (R = CN). This type of fragmentation would not be possible with structure **24**. A complex multiplet consisting of two aliphatic protons at δ 4.3–4.7 in the NMR spectrum also favors structure **23**.

Reaction of **22** with dimethyl acetylenedicarboxylate in boiling xylene gave rise to dimethyl 7,8,11,12-tetraphenylnaphtho[2′,3′:2,3]pyrazolo[1,5-*a*]quinoline-9,10-dicarboxylate (**25**, R = $COOCH_3$), mp 331.5–334 °C, by extrusion of sulfur from the initial 1:1 cycloadduct. Spectral and analytical data were in accord with this structure.

Experimental Section[17]

General Preparative Procedures. A. 2,3-Dibenzoylpyrazolo[1,5-*a*]pyridines (6). Anhydrous K_2CO_3 (18.1 g, 0.131 mol) was added at room temperature to a solution of 1-aminopyridinium iodide (**3**, R = R^1 = H) (26.5 g, 0.119 mol) in DMF (200 mL, distilled over BaO) and the mixture stirred for 30 min during development of a bright-blue color characteristic of ylide formation. Dibenzoylacetylene (27.8 g, 0.119 mol) dissolved in DMF (190 mL) was added dropwise over 1.5 h and the reaction mixture then stirred at room temperature for 14 h. Water (2000 mL) was then added to induce crystallization. After the product was separated and dried (vacuum oven, P_2O_5, 28 °C (20 mm)), the brown powder (34.3 g) was extracted with Et_2O in a soxhlet for 24 h, and the ether solution was decolorized (charcoal) and then evaporated. Crystallization of the orange-yellow residue from isopropyl alcohol afforded glistening, golden-yellow plates: 21.8 g (56%); mp 141.5–142.5 °C. Its spectral characteristics are listed in Table I.

B. 1,4-Diphenylpyrido[1′,2′:2,3]pyrazolo[3,4-*d*]pyridazines (7). Crude 2,3-dibenzoylpyrazolo[1,5-*a*]pyridine (**6a**) (4.0 g, 0.012 mol) was dissolved in anhydrous hydrazine (100 mL) and the resulting solution refluxed for 30 min, during which time a yellow product began to separate from solution. The cooled reaction mixture was filtered, and the separated product was washed with water and then recrystallized from aqueous ethanol affording yellow needles: 2.1 g (53%); mp 226–227 °C dec. These products are described in Table I.

C. 1,3-Diphenylthieno[3,4-*b*]pyrazolo[1,5-*a*]pyridine-2-S^{IV} (8). 2,3-Dibenzoylpyrazolo[1,5-*a*]pyridine (**6a**) (5.0 g, 0.015 mol) and P_4S_{10} (3.40 g, 0.015 mol) were dissolved in freshly distilled pyridine (60 mL) and the solution refluxed for 17 h. The deep orange-red colored solution was poured into ice water (0.6 kg) and glacial acetic acid (5 mL) added. The solid, tarry product was separated and dried in vacuo over P_2O_5. It was then extracted with hot, absolute alcohol (500 mL) which, on cooling, deposited small, brick-red needles: 3.06 g (62%); mp 149.5–150.5 °C. These products are described further in Table I.

(17) All meeting prints were determined in capillaries, using a Thomas-Hoover or a Mel-Temp apparatus. Evaporations were carried out under reduced pressure, using a rotatory evaporator, and spectral characteristics were determined on the following instrumentation: infrared spectra, Perkin-Elmer Models 137, 337, and 467 spectrophotometers; ultraviolet spectra, Cary 15 spectrophotometer; NMR spectra, Varian T-60 and HA-100 spectrometers, using Me_4Si as internal standard; mass spectra, Jeolco JMS-01SC mass spectrometer, utilizing the direct inlet probe with a source temperature of ca. 150 °C. Microanalyses were performed by Instranal Laboratories, Inc., Rensselaer, N.Y., and Galbraith Laboratories, Inc., Knoxville, Tenn. Thin-layer chromatography: materials and apparatus, silica gel F-254 (EM Labs Inc.) and silica gel F 254/366 (Woelm) precoated 0.25-mm plates were used.

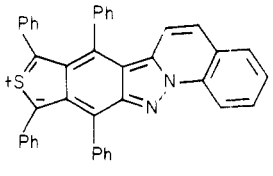
detected during this reaction, and the structure of **19** was readily established from the spectral data.

Both dimethyl acetylenedicarboxylate and dibenzoylacetylene underwent reaction with **16** in refluxing xylene, although extended reaction times were required for complete reaction to occur. The intermediate **20** (R = $COOCH_3$ and COPh, respectively) was undoubtedly involved in the reaction, the final products, dimethyl 7,10-diphenylbenzo[*b*]pyrazolo[1,5-*a*]quinoline-8,9-dicarboxylate (**19**, R = $COOCH_3$) (76%) and 8,9-dibenzoyl-7,10-diphenylbenzo[*b*]pyrazolo[1,5-*a*]quinoline (**19**, R = COPh) (38%), being formed by elimination of sulfur from the appropriately substituted intermediate **20**. Spectral characterization of these two secondary cycloadducts is described below.

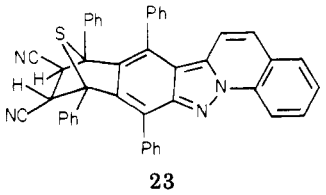
In the isoquinoline series it was not necessary to separate the mixture of 1,2-dibenzoylpyrazolo[5,1-*a*]isoquinoline (**15**) and its dihydro derivative **14** before reaction with P_4SO_{10}/pyridine. 1,3-Diphenylthieno[3′,4′:3,4]pyrazolo-[5,1-*a*]isoquinoline-2-S^{IV} (**21**) was obtained as brick-red, irregular prisms in poor yield. It was always contaminated with unreacted **15** under these reaction conditions, the **15** being readily removed by extraction with hot ethanol. The "nonclassical" thiophene **21** was quite stable in the solid phase, but in solution the deep-red color bleached rapidly. The poor yield of **21** obtained above may be attributed to the severe steric crowding between the 1-phenyl substituent and the benzene ring of the isoquinoline moiety.

7,8,10,11-Tetraphenylthieno[3′,4′:8,9]benzo[*b*]-pyrazolo[1,5-*a*]quinoline-9-S^{IV} (22). 8,9-Dibenzoyl-7,10-diphenylbenzo[*b*]pyrazolo[1,5-*a*]quinoline (**19**, R = COPh) prepared above has two *vic*-benzoyl groups in the appropriate relationship for the formation of a thiophene ring. Accordingly, on treatment of **19** (R = COPh) with P_4S_{10} in refluxing pyridine, **22** was readily formed and isolated as navy-blue, irregular prisms, mp 260–262 °C (63%). This represents the first stable representative of a 22π-electron system containing "tetravalent" sulfur in a five-membered ring. Dilute solutions of **22** were rapidly bleached on exposure to light, probably by addition of oxygen to the thiocarbonyl ylide system.

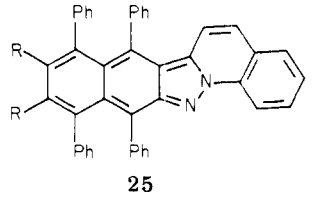
Absorption maxima were observed in the ultraviolet spectrum of **22** at 390 and 310 nm and in the visible at 632 nm. The NMR spectrum consisted of two aromatic multiplets, δ 6.73–7.70 (21 protons) and δ 7.79–8.41 (4 protons), and an aromatic doublet, δ 8.67 (1 proton, J = 8.0 Hz). The most abundant ion in the mass spectrum corresponded to the molecular ion m/e 578 (100%), and the doubly charged molecular ion, m/e 289 (43%), was also evident.



22



23



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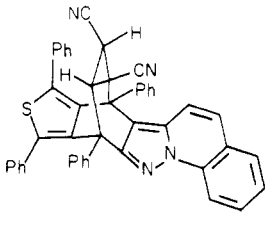

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Treatment of **22** with fumaronitrile in refluxing xylene resulted in the formation of a primary 1:1 cycloadduct, mp 282.5–284.5 °C, isolated as fawn irregular prisms. Two possible structures **23** and **24** were considered for this adduct as addition could occur across either the 8 and 10 positions or the 7 and 11 positions. The mass spectrum showed a low intensity molecular ion m/e 656, with the primary mode of fragmentation being a thermal retro-Diels–Alder reaction to the initial components of the reaction, both being detected in the spectrum. A less prominent mode of electron-impact fragmentation was initiated by loss of the sulfur bridge to give ion m/e 624. Further decomposition by two successive eliminations of hydrogen atoms gave ion m/e 622 which would correspond to **25** (R = CN). This type of fragmentation would not be possible with structure **24**. A complex multiplet consisting of two aliphatic protons at δ 4.3–4.7 in the NMR spectrum also favors structure **23**.

Reaction of **22** with dimethyl acetylenedicarboxylate in boiling xylene gave rise to dimethyl 7,8,11,12-tetraphenylnaphtho[2′,3′:2,3]pyrazolo[1,5-*a*]quinoline-9,10-dicarboxylate (**25**, R = $COOCH_3$), mp 331.5–334 °C, by extrusion of sulfur from the initial 1:1 cycloadduct. Spectral and analytical data were in accord with this structure.

Experimental Section[17]

General Preparative Procedures. A. 2,3-Dibenzoylpyrazolo[1,5-*a*]pyridines (6). Anhydrous K_2CO_3 (18.1 g, 0.131 mol) was added at room temperature to a solution of 1-aminopyridinium iodide (**3**, R = R^1 = H) (26.5 g, 0.119 mol) in DMF (200 mL, distilled over BaO) and the mixture stirred for 30 min during development of a bright-blue color characteristic of ylide formation. Dibenzoylacetylene (27.8 g, 0.119 mol) dissolved in DMF (190 mL) was added dropwise over 1.5 h and the reaction mixture then stirred at room temperature for 14 h. Water (2000 mL) was then added to induce crystallization. After the product was separated and dried (vacuum oven, P_2O_5, 28 °C (20 mm)), the brown powder (34.3 g) was extracted with Et_2O in a soxhlet for 24 h, and the ether solution was decolorized (charcoal) and then evaporated. Crystallization of the orange-yellow residue from isopropyl alcohol afforded glistening, golden-yellow plates: 21.8 g (56%); mp 141.5–142.5 °C. Its spectral characteristics are listed in Table I.

B. 1,4-Diphenylpyrido[1′,2′:2,3]pyrazolo[3,4-*d*]pyridazines (7). Crude 2,3-dibenzoylpyrazolo[1,5-*a*]pyridine (**6a**) (4.0 g, 0.012 mol) was dissolved in anhydrous hydrazine (100 mL) and the resulting solution refluxed for 30 min, during which time a yellow product began to separate from solution. The cooled reaction mixture was filtered, and the separated product was washed with water and then recrystallized from aqueous ethanol affording yellow needles: 2.1 g (53%); mp 226–227 °C dec. These products are described in Table I.

C. 1,3-Diphenylthieno[3,4-*b*]pyrazolo[1,5-*a*]pyridine-2-S^{IV} (8). 2,3-Dibenzoylpyrazolo[1,5-*a*]pyridine (**6a**) (5.0 g, 0.015 mol) and P_4S_{10} (3.40 g, 0.015 mol) were dissolved in freshly distilled pyridine (60 mL) and the solution refluxed for 17 h. The deep orange-red colored solution was poured into ice water (0.6 kg) and glacial acetic acid (5 mL) added. The solid, tarry product was separated and dried in vacuo over P_2O_5. It was then extracted with hot, absolute alcohol (500 mL) which, on cooling, deposited small, brick-red needles: 3.06 g (62%); mp 149.5–150.5 °C. These products are described further in Table I.

(17) All meeting prints were determined in capillaries, using a Thomas-Hoover or a Mel-Temp apparatus. Evaporations were carried out under reduced pressure, using a rotatory evaporator, and spectral characteristics were determined on the following instrumentation: infrared spectra, Perkin-Elmer Models 137, 337, and 467 spectrophotometers; ultraviolet spectra, Cary 15 spectrophotometer; NMR spectra, Varian T-60 and HA-100 spectrometers, using Me_4Si as internal standard; mass spectra, Jeolco JMS-01SC mass spectrometer, utilizing the direct inlet probe with a source temperature of ca. 150 °C. Microanalyses were performed by Instranal Laboratories, Inc., Rensselaer, N.Y., and Galbraith Laboratories, Inc., Knoxville, Tenn. Thin-layer chromatography: materials and apparatus, silica gel F-254 (EM Labs Inc.) and silica gel F 254/366 (Woelm) precoated 0.25-mm plates were used.

D. *N*,7,10-Triphenylbenzo[*b*]pyrazolo[1,5-*a*]pyridine-8,9-dicarboximide (10a). 1,3-Diphenylthieno[3,4-*b*]pyrazolo-[1,5-*a*]pyridine-2-S^{IV} (**8a**) (5.0 g, 0.015 mol) and *N*-phenylmaleimide (2.65 g, 0.015 mol) were refluxed in dry xylene (100 mL) for 12 h during which H_2S was evolved. The cooled reaction mixture deposited a yellow product, **10a**, which crystallized from dioxane (charcoal) as lemon-yellow, irregular prisms: 4.0 g (56%); mp 307–310 °C dec. These products are described in Table I.

E. 2,3-Dicyano-1,4-diphenylbenzo[*b*]pyrazolo[1,5-*a*]-pyridine (11a). 1,3-Diphenylthieno[3,4-*b*]pyrazolo[1,5-*a*]-pyridine-2-S^{IV} (**8a**) (2.0 g, 0.006 mol) and fumaronitrile (1.2 g, 0.015 mol) in xylene (50 mL) were heated under reflux for 11 h, continuous evolution of H_2S occurring. The black residue isolated from the cooled reaction mixture was washed with Et_2O and then dissolved in hot 1,2-dichloroethane (400 mL). After being concentrated to 100 mL and cooled, this solution deposited pale-yellow microneedles of **11a**: 1.0 g (44%); mp 330–333 °C dec. These products are described in Table I.

2,3-Dibenzoylpyrazolo[1,5-*a*]quinoline (13). 1-Aminoquinolinium iodide[16] (2.72 g, 0.01 mol) and dibenzoylacetylene[18] (2.34 g, 0.01 mol) were dissolved in dry DMF (25 mL), and Et_3N (1.3 g) was added to the brown solution which immediately became warm and turned dark red. The reaction mixture was stirred for an additional 15 min and then poured slowly into ice water. A yellow-brown solid separated which was filtered, washed with water, and dried in vacuo, 3.0 g (80%). Recrystallization from 1:1 acetone–ethanol and then from acetone–isopropyl alcohol afforded cream, irregular prisms: mp 155–156 °C; IR (KBr) 3060 (CH), 1670, 1645 (CO) cm^{-1}; λ_{max} (CH_3OH) 350 nm (log ϵ 4.11), 335 (4.18), 323.5 (sh, 4.13), 253 (4.53); NMR ($CDCl_3$) δ 7.14–7.96 (m, 15, aromatic), 8.70 (d, 1, aromatic, J = 8.0 Hz); M^+· 376 (100).

Anal. Calcd for $C_{25}H_{16}N_2O_2$: C, 79.77; H, 4.28; N, 7.44. Found: C, 79.90; H, 4.19; N, 7.23.

1,3-Diphenylthieno[3′,4′:3,4]pyrazolo[1,5-*a*]quinoline-2-S^{IV} (16). 2,3-Dibenzoylpyrazolo[1,5-*a*]quinoline (**13**) (12.0 g, 0.032 mol), phosphorus pentasulfide (7.1 g, 0.032 mol), and dry pyridine (110 mL) were refluxed for 3 h, the reaction flask being covered with aluminum foil to avoid exposing the reaction mixture to light. After the reflux period was completed, the deep-red solution was poured slowly into ice water (1000 mL) containing acetic acid (75 mL) to enhance crystallization. A brick-red solid separated which was filtered, washed with water followed by ethanol, and dried in vacuo, 13.4 g. This material was dissolved in boiling acetone (2400 mL) and a red-black insoluble (0.2 g) was filtered off. After the filtrate was concentrated to approximately 600 mL, isopropyl alcohol (200 mL) was slowly added as to maintain boiling, the solution was concentrated to approximately 550 mL, an additional 200 mL of isopropyl alcohol was added, and the solution was concentrated again. This was repeated a third time using water instead of isopropyl alcohol. The mixture was cooled and brick-red, irregular prisms were filtered, washed with isopropyl alcohol and dried in vacuo, 11.2 g (93%). Recrystallization using the above procedure with acetone–ethanol–water gave brick-red irregular prisms: mp 211.5–213 °C; IR (KBr) 3060 (CH) cm^{-1}; λ_{max} (CH_3OH) 352 (log ϵ 4.20), 335.5 (4.22), 325 (4.17), 285 (4.34), 252.5 nm (4.50); NMR ($CDCl_3$) δ 7.10–8.20 (m, 15, aromatic), 8.89 (d, 1, aromatic, J = 8.0 Hz); M^+· 376 (100), M^{2+} 188 (46).

Anal. Calcd for $C_{25}H_{16}N_2S$: C, 79.75; H, 4.28; N, 7.44. Found: C, 79.72; H, 4.14; N, 7.34.

***N*,7,10-Triphenylbenzo[*b*]pyrazolo[1,5-*a*]quinoline-8,9-dicarboximide (18).** In a 100-mL flask covered with aluminum foil, **16** (1.88 g, 0.005 mol) and *N*-phenylmaleimide (0.87 g, 0.005 mol) were refluxed in xylene (35 mL) for 24 h. After only a few minutes of reflux, evolution of H_2S was detected. After the reaction mixture was cooled in an acetone–ice bath, a yellow precipitate separated, which was filtered, washed with cold xylene, and dried in vacuo, 1.4 g (54%). This was extracted with hot CH_3CN (1 week) in a soxhlet extractor, and the product obtained on cooling the solution was filtered, washed with isopropyl alcohol, and dried in vacuo. Recrystallization (charcoal) from dioxane–water afforded pale yellow, irregular prisms: mp 382–384 °C; IR (KBr) 3820, 3060 (CH), 1760, 1710 cm^{-1} (CO); λ_{max} (CH_3OH) 382, 392 nm; NMR ($ASCl_3$) δ 7.05 (d, 1, aromatic, J = 10.0 Hz), 7.3–8.1 (m, 19, aromatic), 8.81 (d, 1, aromatic, J = 8.0 Hz); M^+· 515 (100).

Anal. Calcd for $C_{35}H_{21}N_3O_2$: C, 81.54; H, 4.11; N, 8.15. Found: C, 81.26; H, 4.25; N, 7.99.

8,9-Dicyano-7,10-diphenylbenzo[*b*]pyrazolo[1,5-*a*]-quinoline (19, R = CN). In a 100-mL flask covered with aluminum foil, **16** (1.88 g, 0.005 mol) and fumaronitrile (0.40 g, 0.005 mol) were refluxed for 10 h in xylene (35 mL). The evolution of H_2S was quickly detected once heating was commenced. The reaction was cooled in an acetone–ice bath, and the brown precipitate was filtered, washed with cold xylene, and dried in vacuo, 1.43 g (68%). An analytically pure sample was prepared by a Soxhlet extraction for 1 week, using dioxane as the solvent. After concentrating the solution in vacuo, water was added to aid precipitation, and the collected precipitate (R_f 0.6) was recrystallized (charcoal) from aqueous dioxane, affording pale-yellow, irregular prisms: mp 398–400 °C; IR 3040 (CH), 2220 (CN) cm^{-1}; λ_{max} (CH_3OH) 410, 387.5, 361, 313, 298, 285 nm; NMR ($AsCl_3$) δ 7.08 (d, 1, aromatic J = 9.6 Hz), 7.6–8.1 (m, 14, aromatic), 8.85 (d, 1, aromatic, J = 8.0 Hz); M^+· 420 (100).

Anal. Calcd for $C_{29}H_{16}N_4$: C, 82.84; H, 3.84; N, 13.33. Found: C, 82.42; H, 4.10; N, 13.60.

Dimethyl 7,10-Diphenylbenzo[*b*]pyrazolo[1,5-*a*]-quinoline-8,9-dicarboxylate (19, R = $COOCH_3$). In a 100-mL flask covered with aluminum foil, **16** (1.88 g, 0.005 mol) and dimethyl acetylenedicarboxylate (0.83 g, 0.005 mol) were refluxed for 23 h. TLC ($CHCl_3$ system) showed (at R_f 0.9) **16** was still present, and the cycloadduct appeared at R_f 0.1. Additional dimethyl acetylenecarboxylate (1.0 g, 0.071 mol) was added, and the solution was refluxed for an additional 23 h. The solution was cooled in an acetone–ice bath, a few dark grains were filtered, and the filtrate was allowed to evaporate to a dark sticky residue (3.3 g). This residue was dissolved in boiling acetone (100 mL), and sulfur (0.5 g) was filtered off. The filtrate was heated to boiling and water (25 mL) added. After the solution was cooled to room temperature, the product was filtered, washed with water, and dried in vacuo, 1.85 g (76%). After four recrystallizations, the product, 1.0 g (41%), was obtained as tan needles: mp 221.5–222.5 °C; IR (KBr) 3000 (CH), 1710 (CO) cm^{-1}; λ_{max} (CH_3OH) 396.5 (log ϵ 4.11), 378 (4.10), 359 (3.97), 310 (4.17), 295 (4.23), 275 nm (4.55); NMR ($CDCl_3$) δ 3.56 (s, 3, CO_2CH_3), 3.63 (s, 3, CO_2CH_3), 6.74 (d, 1, aromatic, J = 9.6 Hz), 7.21–7.84 (m, 14, aromatic), 8.84 (d, 1, aromatic, J = 8.0 Hz); M^+· 486 (100).

Anal. Calcd for $C_{31}H_{22}N_2O_4$: C, 76.53; H, 4.56; N, 5.76. Found: C, 76.17; H, 4.64; N, 5.61.

8,9-Dibenzoyl-7,10-diphenylbenzo[*b*]pyrazolo[1,5-*a*]-quinoline (19, R = COPh). In a 250-mL flask covered with aluminum foil, **16** (3.76 g, 0.01 mol) and dibenzoylacetylene (2.34 g 0.01 mol) were refluxed for 1 week in xylene (140 mL). The solution was evaporated to dryness on the rotovap, and TLC ($CHCl_3$ system) showed no dibenzoylacetylene but a considerable amount of unreacted **16**. This residue was dissolved in xylene (140 mL) and refluxed for an additional week with additional dibenzoylacetylene (0.8 g, 0.0034 mol). The solution was then evaporated to dryness in vacuo and dissolved in boiling acetone (75 mL). Sulfur (0.87 g) was filtered off, the filtrate was concentrated at atmospheric pressure to approximately 50 mL, and isopropyl alcohol (100 mL) was added slowly to maintain boiling. The mixture was concentrated to 75 mL and cooled and the separated material filtered. After two additional crystallizations (charcoal), the product was obtained as fine, golden-brown needles: 2.2 g (38%); mp 256.5–258.5 °C; IR (KBr) 3080 (CH), 1640 (CO) cm^{-1}; λ_{max} (CH_3OH) 404 nm (log ϵ 4.17), 385 (4.15), 365 (4.11), 294 (4.61), 253 (4.71), 232 (4.59); NMR ($CDCl_3$) δ 6.85–7.9 (m, 25, aromatic), 8.9 (d, 1, aromatic, J = 7.7 Hz); M^+· 578 (37).

Anal. Calcd for $C_{41}H_{26}N_2O_2$: C, 85.09; H, 4.53; N, 4.84. Found: C, 84.60; H, 4.63; N, 4.93.

5,6-Dihydro-1,2-dibenzoylpyrazolo[5,1-*a*]isoquinoline (14). 2-Aminoisoquinolinium iodide (13.60 g, 0.05 mol) and dibenzoylacetylene (11.70 g, 0.05 mol) were dissolved in dry DMF (125 mL), and Et_3N (10.0 g) was added to the dark-brown solution which immediately became warm and turned dark red in color. The reaction was stirred for 1.5 h at which time a red precipitate was evident. TLC ($CHCl_3$ system) showed strong spots at R_f 0.0, 0.1, and 0.3 and no unreacted dibenzoylacetylene. The mixture was poured slowly into ice water and the orange-red solid which separated was filtered, washed with water, and dried in vacuo;

(18) White, J. D.; Mann, M. E.; Kirshbaum, H. D.; Mitra, M. *J. Org. Chem.* **1971**, *36*, 1048.

20.0 g. Recrystallization of 5.0 g of the above material from acetonitrile (250 mL) (charcoal) gave a crude yield of 3.82 g (81%). TLC ($CHCl_3$ system) showed two reaction products at R_f 0.4 and 0.1. This material consisted of fine orange needles and red rhombic prisms, which when separated manually proved to be two distinct compounds in approximately equal amounts. Approximately 0.4 g of these crude products was separated and purified by preparative TLC ($CHCl_3$ system), and each component was dissolved in hot chloroform. The filtrates were concentrated to 20 mL at which point acetonitrile (50 mL) was added slowly to maintain boiling. The solution was concentrated at atmospheric pressure to 20 mL, and the acetonitrile addition and concentration was repeated three more times to a final volume of 10 mL. Water (10 mL) was added, and the solution was cooled affording orange-red, irregular prisms from the material appearing at R_f 0.4: mp 192–194.5 °C; IR (KBr) 3070 (CH), 1675 (CO) cm^{-1}; λ_{max} (CH_3OH) 427 nm (log ϵ 4.18), 257 (4.40); NMR (CF_3COOD) δ 7.00–8.67 (m, 16, aromatic), four ill-defined peaks in the range 4.0–6.2, integrating for approximately 1 proton, were observed: M^+· 378 (2), 376 (6), 105 (100), 188 (1).

Anal. Calcd for $C_{25}H_{18}N_2O_2$: C, 79.35; H, 4.79; N, 7.40. Found: C, 79.59; H, 4.51; N, 7.42.

1,2-Dibenzoylpyrazolo[5,1-*a*]isoquinoline (15). Isolated by preparative TLC as described above from the material appearing at R_f 0.1 were pale-yellow, irregular prisms which corresponded to the red rhombic prisms: mp 222–223.5 °C; IR (KBr) 3065 (CH), 1665 (CO) cm^{-1}; λ_{max} (C_2H_6SO) 435 nm (log ϵ 3.08), 340 (inflection point) (3.80), 325 (sh, 3.88), 2.80 (4.41); NMR (CF_3COOD) δ 7.25–8.23 (m, 14, aromatic), 8.44 (dd, 1, aromatic, J = 8.0, 2.0 Hz), 8.70 (d, 1, aromatic, J = 7.5 Hz); M^+· 376 (32), 188 (4), 105 (100).

Anal. Calcd for $C_{25}H_{16}N_2O_2$: C, 79.77; H, 4.28; N, 7.44. Found: C, 79.65; H, 4.25; N, 7.50.

7,8-Dihydro-1,4-diphenylpyridazino[4′,5′:1,2]pyrazolo[5,1-*a*]isoquinoline. 5,6-Dihydro-1,2-dibenzoylpyrazolo[5,1-*a*]isoquinoline (**14**) (0.2 g, 0.00053 mol) and hydrazine (45 mL) were refluxed overnight in ethanol (15 mL). The clear yellow solution was concentrated to dryness and the residue recrystallized from aqueous acetone to afford 0.04 g (20%) of pale-yellow, irregular prisms: mp 295–298 °C; IR (KBr) 3040 (CH) cm^{-1}; NMR (CF_3COOD) δ 3.47 (t, 2, aliphatic, J = 7.0 Hz), 4.92 (t, 2, aliphatic, J = 7.0 Hz), 6.49 (d, 1, aromatic, J = 7.4 Hz), 6.8–7.24 (m, 1, aromatic), 7.46 (d, 2, aromatic, J = 5.0 Hz), 7.58–8.20 (m, 8, aromatic), 8.4–8.6 (m, 2, aromatic); M^+· 374 (74), 373 (100). This system was readily oxidized and attempted recrystallizations failed to produce an analytically pure sample.

1,4-Diphenylpyridazino[4′,5′:1,2]pyrazolo[5,1-*a*]isoquinoline. 1,2-Dibenzoylpyrazolo[5,1-*a*]isoquinoline (**15**) (0.65 g, 0.00173 mol) and hydrazine (50 mL) were refluxed overnight in ethanol (18 mL). The mixture was cooled and filtered and the product air dried; 0.55 g (85%). An analytically pure sample was prepared by dissolving the above in acetone (100 mL) and chloroform (300 mL) and concentrating to 175 mL. Ethanol (100 mL) was added slowly, maintaining boiling, and the solution was concentrated to 150 mL yielding 0.50 g of pale-yellow, irregular prisms: mp 353.5–355.5 °C; IR (KBr) 3055 (CH) cm^{-1}; λ_{max} ($CHCl_3$) 377 nm (log ϵ 4.46), 295 (4.75), 273 (inflection point) (4.58); NMR (CF_3COOD) δ 7.15 (d, 1, aromatic, J = 8.4 Hz), 7.32–8.73 (m, 14, aromatic), 9.05 (d, 1, aromatic, J = 7.2 Hz); M^+· 372 (82), 371 (100).

Anal. Calcd for $C_{25}H_{16}N_4$: C, 80.62; H, 4.33; N, 15.05. Found: C, 80.40; H, 4.48; N, 15.13.

1,3-Diphenylthieno[3′,4′:3,4]pyrazolo[5,1-*a*]isoquinoline-2-S^{IV} (21). A mixture of 5,6-dihydro-1,2-dibenzoylpyrazolo[5,1-*a*]isoquinoline (**14**) and 1,2-dibenzoylpyrazolo[5,1-*a*]isoquinoline (**15**) (3.76 g, 0.01 mol), previously slurried in boiling ethanol to remove some 1,2-dibenzoylpyrazolo[5,1-*a*]isoquinoline, and phosphorus pentasulfide (2.22 g, 0.01 mol) were refluxed in dry pyridine (40 mL) as above for 3 h, a color change from orange to red occurring over this period. The cooled solution was poured slowly into ice water (600 mL) containing acetic acid (25 mL) to enhance crystallization. The brick red precipitate was filtered, washed with water, and dissolved in boiling acetone (800 mL). The hot solution was filtered to remove trace insolubles and concentrated to 225 mL. Ethanol, 92% (300 mL), was added, maintaining boiling, and the mixture was then concentrated to 275 mL and cooled to room temperature and the product filtered the next day and washed with ethanol; 2.5 g (67%). This crude **21** contained some residual **15** which was removed by four successive slurries in boiling 92% ethanol (approximately 200 volumes). An analytically pure sample was prepared by recrystallization of this material (0.55 g) from acetone–isopropyl alcohol, affording 0.4 g of small red matted needles: mp 229–231 °C; IR (KBr) 3050, 3100 (CH) cm^{-1}; λ_{max} (CH_3OH) 495 nm (log ϵ 4.36), 386 (3.75), 333 (4.40), 262 (4.32), 233 (4.55); NMR (CF_3COOD) δ 7.18–8.32 (m, 15, aromatic), 8.73 (d, 1, aromatic, J = 7.0 Hz); M^+· 376 (100), M^{2+}, 188 (33).

Anal. Calcd for $C_{25}H_{16}N_2S$: C, 79.75; H, 4.28; N, 7.44. Found: C, 79.78; H, 4.29; N, 7.33.

7,8,10,11-Tetraphenylthieno[3′,4′:8,9]benzo[*b*]pyrazolo[1,5-*a*]quinoline-9-S^{IV} (22). 8,9-Dibenzoyl-7,10-diphenylbenzo[*b*]pyrazolo[1,5-*a*]quinoline (**19**, R = COPh) (4.3 g, 0.0075 mol) and phosphorus pentasulfide (1.7-g, 0.0077 mol) were refluxed in dry pyridine (75 mL) as above for 23 h. The deep blue solution was cooled to room temperature and a small amount of dark material removed. The solution was then added slowly to ice water (approximately 1000 mL) containing acetic acid to enhance crystallization. The product was filtered, washed with water, and recrystallized from a large volume of aqueous acetone, giving 2.7 g (63%) of air-dried product. Recrystallization from acetone–isopropyl alcohol afforded navy-blue, irregular prisms: mp 260–262 °C dec; IR (KBr) 3040 (CH) cm^{-1}; λ_{max} (C_2H_6SO) 632 nm (log ϵ 4.16), 390 (4.35), 310 (4.50); NMR ($CDCl_3$) δ 6.73–7.70 (m, 21, aromatic), 7.79–8.41 (m, 4, aromatic), 8.67 (d, 1, aromatic, J = 8.0 Hz); M^+ – 578 (100), M^{2+} 289 (43).

Anal. Calcd for $C_{41}H_{26}N_2S$: C, 85.09; H, 4.53; N, 4.84. Found: C, 85.19; H, 4.52; N, 4.74.

Reaction of 22 with Fumaronitrile. Fumaronitrile (0.15 g, 0.0019 mol) and **22** (0.58 g, 0.001 mol) were refluxed in xylene (25 mL) for 24 h as above. TLC ($CHCl_3$ system) showed no **22** remaining. A small amount of insolubles was filtered off, and the filtrate was evaporated to dryness. The residue was dissolved in boiling chloroform (25 mL), and 92% ethanol (75 mL) was added slowly to maintain boiling. The solution was concentrated, and the procedure was repeated a third time. The solution was cooled at 5 °C for several days, filtered, and washed with ethanol, giving a crude yield of 0.45 g (68%) of product. The above recrystallization was repeated twice more using chloroform, isopropyl alcohol, and a small amount of water to aid crystallization. The product still showed trace impurities by TLC which were removed by two more recrystallizations utilizing chloroform and ethanol, affording fawn, irregular prisms: mp 282.5–284.5 °C; IR (KBr) 3030, 3060 (CH), 2250 w (CN) cm^{-1}; λ_{max} ($CHCl_3$) 393 nm (log ϵ 4.26), 373 (4.24), 357 (4.12), 308 (4.30), 296 (4.46), 285 (4.61), 261 (4.51); NMR ($CDCl_3$) 4.3–4.7 (m, 2, aliphatic), 6.0 (dd, 1, aromatic, J = 9.5 and 2.5 Hz), 6.65–7.8 (m, 24, aromatic), 8.6, (d, 1, aromatic, J = 8.0 Hz); M^+· 656 (1), 624 (1), 622 (2), 578 (100).

Anal. Calcd for $C_{45}H_{28}N_4S$: C, 82.29; H, 4.29; N, 8.53. Found: C, 82.02; H, 4.46; N, 8.54.

Dimethyl 7,8,11,12-Tetraphenylnaphtho[2′,3′:2,3]pyrazolo[1,5-*a*]quinoline-9,10-dicarboxylate (25, R = $COOCH_3$). Dimethyl acetylenedicarboxylate (0.30 g, 0.002 mol) and **22** (0.58 g, 0.001 mol) were refluxed in xylene (50 mL) for 24 h as above. TLC ($CHCl_3$ system) showed **22** remaining (R_f 0.5) with the reaction product appearing at R_f 0.1. Dimethyl acetylenedicarboxylate (0.6 g, 0.0042 mol) was added, and the reaction was refluxed for an additional 96 h. TLC ($CHCl_3$ system) showed only a trace amount of **22**, a large amount of reaction product at R_f 0.1 and a small amount of impurity at R_f 0.8. A small amount of insolubles was filtered from the dark-green solution, and the filtrate was concentrated to dryness in vacuo. The residue was dissolved in boiling chloroform (25 mL), and 92% ethanol (75 mL) was added slowly to maintain boiling. The solution was concentrated at atmospheric pressure to 25 mL, and two more 92% ethanol additions followed by concentrating were performed. This was repeated a fourth time with isopropyl alcohol affording 0.4 g (58%) of crude dimethyl 7,8,11,12-tetraphenylnaphtho[2′,3′:2,3]pyrazolo[1,5-*a*]quinoline-9,10-dicarboxylate (**25**, R = $COOCH_3$). Repeated recrystallization from $CHCl_3$–EtOH afforded orange, irregular prisms: mp 331.5–334 °C; IR (KBr) 2950, 3070 (CH), 1720 (CO) cm^{-1}; λ_{max} ($CHCl_3$) 510 nm (log ϵ 4.08), 482 (4.09), 422 (3.77), 350 (inflection point) (4.44), 342 (4.45), 310 (inflection point) (4.64), 299 (4.66), 249 (4.55); NMR ($CDCl_3$ + 3 drops

Me_2SO-d_6) δ 3.33 (s, 3, CO_2CH_3), 3.38 (s, 3, CO_2CH_3), 6.27 (d, 1, aromatic, J = 9.3 Hz), 6.98–7.97 (m, 24, aromatic), 8.84 (d, 1, aromatic, J = 8.2 Hz); M^+· 688 (100).

Anal. Calcd for $C_{47}H_{32}N_2O_4$: C, 81.96; H, 4.68; N, 4.07. Found: C, 82.04; H, 4.87; N, 4.01.

Registry No. 3a, 6295-87-0; **3b**, 7583-90-6; **3c**, 7583-92-8; **6a**, 71870-12-7; **6b**, 71870-13-8; **6c**, 71870-14-9; **7a**, 71870-15-0; **7b**, 71870-16-1; **7c**, 71870-17-2; **8a**, 71870-18-3; **8b**, 71870-19-4; **8c**, 71870-20-7; **10a**, 71870-21-8; **10b**, 71870-22-9; **10c**, 71870-23-0; **11a**, 71870-24-1; **13**, 71870-25-2; **14**, 71870-26-3; **15**, 71870-27-4; **16**, 71870-28-5; **18**, 71870-29-6; **19** (R = CN), 71870-30-9; **19** (R = $COOCH_3$), 71870-31-0; **19** (R = COPh), 71870-32-1; **21**, 71870-33-2; **22**, 71870-34-3; **23**, 71870-35-4; **25** (R = $COOCH_3$), 71870-36-5; dibenzoylacetylene, 1087-09-8; *N*-phenylmaleimide, 941-69-5; 1-aminoquinolinium iodide, 7170-16-3; fumaronitrile, 764-42-1; dimethyl acetylenedicarboxylate, 762-42-5; 2-aminoisoquinolinium iodide, 40339-95-5; 7,8-dihydro-1,4-diphenylpyridazino[4′,5′:1,2]-pyrazolo[5,1-*a*]isoquinoline, 71870-37-6; 1,4-diphenylpyridazino-[4′,5′:1,2]pyrazolo[5,1-*a*]isoquinoline, 71870-38-7.

Theoretical Ab Initio SCF Investigation on the Photochemical Behavior of the Three-Membered Rings. 6. Aziridine[1]

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Ab initio SCF–CI methods have been used to calculate the potential energy curves corresponding to the ground and low-lying states of the aziridine system when various reaction paths are simulated. They concern three topics: the CC and CN bond rupture ring opening, the formation of carbene and nitrene, the NH bond rupture. The main results are the following: in the gas phase, the CN ring opening is favored while in protic condensed media CC ring opening competes; the nitrene formation is easier in a two-step procedure than in a synchronous two-bond scission while it is the reverse for carbene formation; the unimolecular NH bond rupture is not a primary process in the formation of molecular hydrogen from aziridine. The difference between gas-phase and condensed-protic-phase reactivity is explained by the role played by Rydberg and hydrogen-bond electronic-transfer states.

The photochemical behavior of aziridine and aziridine derivatives is rather complex as shown by numerous experimental works reported in the literature.[3] The nature and distribution of the resulting products strongly differ whether the reaction is carried out in gas or condensed phase.

In the gas phase, aziridine breaks into a variety of products such as molecular hydrogen and nitrogen, ethylene, ammonia, saturated hydrocarbons, and a dimer of the ethylenimino radical.[4,5] Their relative abundance sharply depends on experimental conditions. For example, under static conditions,[5a,c] a great amount of ammonia is produced, but no nitrile compounds are formed (the last assertion is denied by some authors).[3b,6] In a fast-flow system,[5b] however, nitrile compounds have been clearly identified, and the ammonia production is less than in the preceding conditions. Various primary processes[4,5] have been proposed to explain the nature and relative importance of the photodecomposition products, including nitrene extrusion and NH bond rupture. No process, however, involves CC bond rupture.

In the condensed phase, particularly in alcoholic solution, two primary processes are well documented. The first one is deamination[7] which corresponds to the nitrene extrusion previously mentioned for the gas-phase reaction. The second corresponds to a CC bond rupture ring opening.[8] It yields one to three dipolar ylides which can be trapped with various dipolarophiles,[8a] exhibit photochromic properties,[8b] or undergo further fragmentation leading to carbene and imine species.[8c] These fragments differ from those obtained in the gas phase. It appears that polar solvents favor the last evolution—CC bond rupture.

Thus, although several extended experimental studies have been devoted to the subject, the photochemical primary processes of aziridine are not fully ascertained, and the influence of factors such as substitution or solvation is not completely understood.

The subject of this paper is to try to get some new insights on the intimate behavior of the photochemically excited aziridine system by theoretical ab initio SCF–CI investigation. The reactions which will be considered are depicted in Figure 1.

The first simulated transformations are the openings of the three-membered ring by CC bond rupture. Indeed, according to Woodward–Hoffmann denomination,[3] three main modes are to be considered: the face to face (path a), the conrotatory (path b), and the disrotatory (path c) processes. The first mode leads to the formation of intermediate I′ while the last two ones lead to the formation of the same planar intermediate (I). In order to solve the dichotomy concerning the CC reactivity in the gas and in the protic condensed phases, paths a′, b′ and c′ have been simulated. They represent the same transformations as paths a, b, and c, respectively, in presence of a proton in

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