g, 2 mmol) and trimethyl ethylenetricarboxylate (2; 0.404 g, 2 mmol) in 1,2-dichloroethane (4 mL) yielded homopolymer 4 (4.7%) and a mixture of the 1,3 cis and trans isomers of the cyclobutane adduct 3 (38.9%), which precipitated out of hexane at -78 °C as an oil. Anal. Calcd for $C_{24}H_{25}O_6N$: C, 6.81; H, 6.0; N, 3.3. Found: C, 67.8; H, 6.1; N, 2.9.

The two isomers were isolated by column chromatography, using silica gel and hexane as eluent: IR ($CDCl_3$) 2940 (m, CH), 1730 (s, C=O), 1600 cm^{-1} (m, C=C); for isomer **3a**, ^1H NMR ($CDCl_3$) δ 1.4 (t, 3 H, CH_3), 2.87 (m, J = 10 Hz, 2 H, CH_2), 3.1, 3.77 (3 s, 9 H, OCH_3), 4.32 (m, 3 H, NCH_2 and $CHCO_2CH_3$), 4.8 (t, J = 10 Hz, 1 H, HCAr), 7.2-8.2 (m, 7 H, aromatic); for isomer **3b**, ^1H NMR ($CDCl_3$) δ 1.5 (t, 3 H, CH_3), 2.65-3 (m, J = 14 Hz, 2 H, CH_2), 3.23, 3.83, 3.97 (3 s, 9 H, OCH_3), 3.33-3.8 (m, J = 14 Hz, 2 H, CHAr and $CHCO_2CH_3$), 4.3 (q, 2 H, NCH_2) 7.2-8.2 (m, 7 H aromatic).

Poly(*N*-ethyl-3-vinylcarbazole) (4). In a quartz tube, a mixture of 0.433 g (2 mmol) of *N*-ethyl-3-vinylcarbazole (1) and 0.01 g of the 1,4-dicyanobenzene was dissolved in 4 mL of acetonitrile. The reaction vessel was irradiated by UV light in a reactor for 69 h. Formation of a precipitate occurred. The mixture was dripped into 90 mL of anhydrous ether. The mixture was filtered to yield 0.248 g (56.0%) of homopolymer 4[11,16] (the filtrate contained only starting material). The homopolymer was insoluble in acetone, acetonitrile, ether, and methanol: IR (KBr) 2900 (m, CH), 1600 cm^{-1} (m, C=C); ^1H NMR ($CDCl_3$) δ 0.3-2.6 (m, 6 H, CH_3, CH_2, CH), 3.3-4.4 (m, 2 H, NCH_2), 5.5-8.3 (m, 7 H, aromatic). Anal. Calcd for $C_{16}H_{15}N$: C, 86.8; H, 6.8; N, 6.3. Found: C, 85.6; H, 6.8; N, 6.0.

Poly(*N*-ethyl-3-vinylcarbazole-*alt*-trimethyl ethylenetricarboxylate) (5). A mixture composed of 0.404 g (2 mmol) of triester, 0.443 g (2 mmol) of *N*-ethyl-3-vinylcarbazole, and 0.01 g of azobis(isobutyronitrile) (AIBN) was dissolved in 4 mL of benzene, cooled in a dry ice-acetone bath, and degassed under full vacuum. The reaction vessel was placed in an oil bath at 72 °C for 45 h. The reaction was quenched with 100 mL of methanol; the precipitate was separated by filtration, washed, and dried to yield 0.652 g (77.0%) of copolymer 5. The filtrate after workup contained 0.128 g (15.1%) of cyclobutane adduct 3 and starting material: IR (KBr) 2940 (m, CH), 1720 (s, C=O), 1600 cm^{-1} (m, C=C); ^1H NMR ($CDCl_3$) δ 1-1.6 (m, 3 H, CH_3), 2-4.7 (m, 15 H), 6.5-8.5 (m, 7 H, aromatic). Anal. Calcd for $C_{24}H_{25}O_6N$: C, 68.1; H, 6.0; N, 3.3. Found C, 68.4; H, 5.97; N, 3.52.

Dimethyl 1-(*N*-Ethyl-3-carbazyl)-2-cyano-2,3-cyclobutanedicarboxylate (7). A mixture of 0.222 g (1 mmol) of 1 and 0.169 g (1 mmol) of dimethyl cyanofumarate (8) was reacted neat for 16.5 h at room temperature. After workup, a mixture of only two isomers (1,3 cis and 1,3 trans) of the cyclobutane adduct 7 was obtained in 91.8% yield: IR (KBr) 2960 and 2945 (m, CH), 2240 (w, CN), 1740 (s, C=O), 1620, 1590 cm^{-1} (s, C=C). Anal. Calcd for $C_{23}H_{22}N_2O_4$: C, 70.8; H, 5.7; N, 7.2. Found: C, 70.9; H, 5.6; N, 7.1.

One isomer crystallized in hexane at room temperature, and the solution contained both isomers. Isomer **7a** was recrystallized from hexane: mp 144.5-145.5 °C; ^1H NMR ($CDCl_3$) 1.4 (t, 3 H, CH_3), 2.75-3.1 (m, 2 H, CH_2), 3.2, 3.8 (2 s, 6 H, OCH_3), 4.2-4.5 (7, 4 H, CH_2N, $CHCOOCH_3$, and CHAr), 7.2-8.25 (m, 7 H, aromatic) (1,3-cis isomer).

At -78 °C in hexane, a mixture of both isomers precipitated, while the solution contained pure isomer **7b**, which was an oil: ^1H NMR ($CDCl_3$) δ 1.4 (t, 3 H, CH_3), 2.45-3.35 (2 t, J = 10 Hz, 2 H, CH_2), 3.85, 3.9 (2 s, 6 H, OCH_3), 4.3 (m, 4 H, CH_2N, CHAr, $CHCO_2CH_3$), 7.1-8.25 (m, 7 H, aromatic) (1,3-cis isomer).

Tetramethyl 1-(*N*-Ethyl-3-carbazyl)-2,2,3,3-cyclobutanetetracarboxylate (9). A mixture of 1 (0.222 g, 1 mmol) tetramethyl ethylenetetracarboxylate (8; 0.260 g, 1 mmol) in 1,2-dichloroethane (2 mL) was reacted under vacuum at 130 °C for 21.5 h. After removal of the solvent, 30 mL of methanol was added and at -78 °C unreacted tetraester crystallized out. After filtration and evaporation of methanol, the residue was dissolved in 40 mL of hexane and placed at -78 °C to yield the cyclobutane adduct 9 as an oil. Under vacuum crystals are obtained (0.312 g, 64.8%): mp 68-70 °C; IR ($CDCl_3$) 2925 (w, CH), 1720 (s, C=O), 1600 cm^{-1} (w, C=C); ^1H NMR ($CDCl_3$) δ 1.42 (t, 3 H, CH_3), 2.68 (m, 2 H, CH_2), 3.15, 3.85, 3.15, 3.85, 3.9 (3 s, 12 H, OCH_3), 4.35 (q, 2 H, NCH_2), 4.82 (q, 1 H, J = 12 Hz, CH), 7.22-8.2 (m, 7 H, aromatic). Anal. Calcd for $C_{26}H_{27}O_8N$: C, 64.85; H, 5.65; N, 2.91. Found: C, 64.61; H, 5.82; N 2.86.

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Registry No. 1, 1486-07-3; 2, 51175-48-5; *cis*-3, 79917-22-9; *trans*-3, 79917-23-0; 4, 25569-45-3; 5, 79917-26-3; 6, 54797-29-4; 7 (isomer 1), 79917-24-1; 7 (isomer 2), 79980-56-6; 8, 1733-15-9; 9, 79917-25-2.

Studies on Paraionic Compounds. Anhydro-1-hydroxy-3-oxopyrazolo[1,2-*a*]pyrazolium Hydroxides. Formation and Stability of a Novel Series of $4n\pi$ Heterocyclic Betaines

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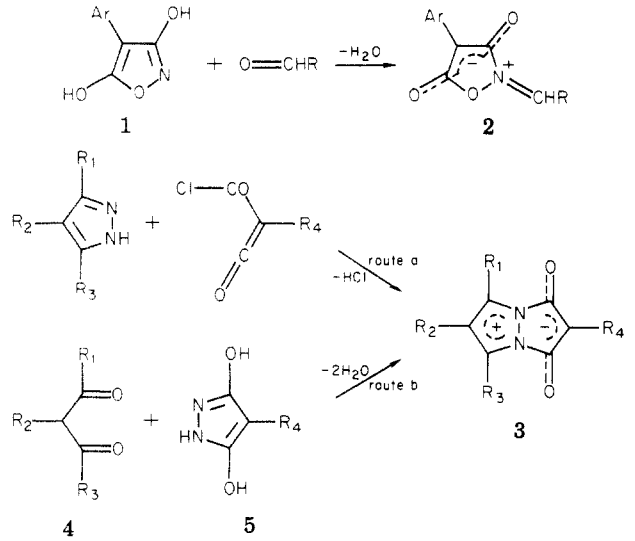
Different substituted anhydro-1-hydroxy-3-oxopyrazolo[1,2-*a*]pyrazolium hydroxides were prepared by the reaction of 1,3-dicarbonyl compounds with derivatives of 4-phenyl-3,5-dihydroxypyrazole. These diazapentalene derivatives belong to a new series of $4n\pi$ cyclic betaines which are named "paraionic" heterocycles. The effects of substituents on the stability of both the anionic and the cationic rings were kinetically studied. Selective cleavage of either the anionic or the cationic ring was achieved by varying the conditions of the reaction with morpholine. Electron releasing groups on the cationic ring and electron attracting groups on the anionic ring enhance the stability of the bicyclic system. They also cause a hypsochromic shift of the visible light absorption.

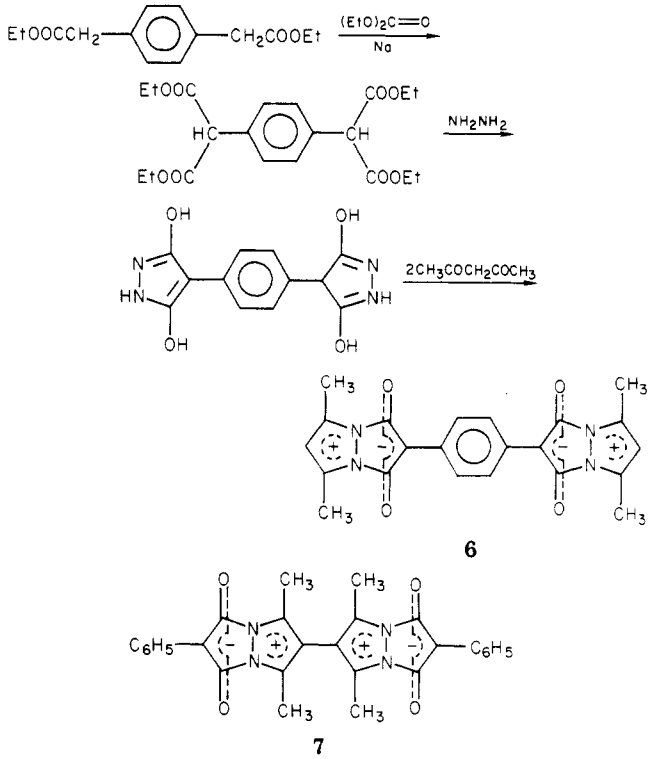
The term paraionic is derived from the observation that both the anion and the cation coexist parallel to one another with the absence of conjugation between them. There is, however, some interaction which is responsible for the extra stability as well as the color and deserves further study. The first group of this series was reported[1]

0022-3263/82/1947-0295$01.25/0

Scheme I



Scheme II



in 1972. These were the monocyclic $4n\pi$ heterocyclic betaines, e.g., *N*-(arylmethylidene)-4-phenylisoxazol-5-onium enolates (**2**). They were formed by the spontaneous condensation of aldehydes with 4-phenyl-3,5-dihydroxyisoxazole (**1**). This group was expanded later,[2,3] and the products were named aldisates.[3] The same compounds were recently[4,5] synthesized by the reaction of α-(chlorocarbonyl)phenylketene with aldoximes and ketoximes. In these reports[4,5] and in a later repetition[6] α-(chlorocarbonyl)phenylketene as well as malonyl chlorides were allowed to react with pyrazoles to form the bicyclic diazapentalene analogues, e.g., anhydro-1-hydroxy-3-oxopyrazolo[1,2-*a*]pyrazolium hydroxides (**3**). The name $4n\pi$ mesoionic heterocycles was also suggested;[6] however, the term mesoionic should be reserved to the already known aromatic mesoionic heterocycles, and we prefer the term "paraionic heterocycles" which was suggested earlier.[4,5] The anionic ring as well as the whole system are nonaromatic, and the linkage between the two ionic rings is not stabilized by conjugation as demonstrated by the long C_1–N_8 and C_3–N_4 bonds (1.49 Å), derived from X-ray diffraction studies.[5] More evidence for such features can be found in the previous[3] study on the monocyclic system as well as in the present work.

Synthesis and Spectra of Substituted Anhydro-1-hydroxy-3-oxopyrazolo[1,2-*a*]pyrazolium Hydroxides. The previously described syntheses[4-6] were based on the highly reactive chloride or ketene (route a, Scheme I), while in the present work the formation of the betaines **3** was accomplished by the condensation of 1,3-dicarbonyl compounds with the rather stable 4-phenyl-3,5-dihydroxypyrazole and its derivatives (**5**,[7] route b). This condensation seems to be a thermodynamically controlled reaction in which a $4n + 2$ electron system (**5**) is transformed into a $4n\pi$ system by loss of two molecules of water. The reaction takes place either by heating of **4** plus **5** for a short period (5 min) or by keeping the mixture at room temperature for 1–2 h. Its facility is indicative of the relative thermodynamic stability of the new bicyclic system. The reaction did not require any catalysis; diketones and dialdehydes reacted spontaneously. In cases where aldehydes had to be generated from the acetal derivatives, the presence of acid, preferably aqueous HCl, was necessary. When dibenzoylmethane was used, condensation did not take place, probably because of steric hindrance. Such products (**3**, $R_1 = R_3 = C_6H_5$) were prepared, when needed for comparison, by route a[4] (Scheme I). Tricyclic systems could be obtained by using 2-acetylcyclopentanone or 2-acetylcyclohexanone.

The C–H stretching absorption in the pyrazolium ring of these betaines is found at a relatively high frequency, e.g., 3140 cm^{-1}, and that of the C=O is found within 1640–1700 cm^{-1}, a range which is more than 100 cm^{-1} lower than that observed[3] in the monocyclic derivatives (1760–1800 cm^{-1}). The visible absorption is in general at shorter wavelengths than that in the monocyclic analogues (460–525 nm) but longer than that in the extremely stable *p*-(dimethylamino)benzaldisate[3] (415 nm). The extinction coefficient is of the order of 10^3 (Table I). Substituents which stabilize the molecule, e.g., electron-donating groups on the cation and electron-attracting groups on the anion, shift the maxima in the visible toward shorter wavelengths (see Table I). A huge blue shift is observed in the *p*-nitrophenyl derivatives (**3j–l**) where the visible absorption coalesces with that in the UV region. The latter is shifted to longer wavelengths and the joint maximum is at 375 nm (in CH_3CN). It is pertinent to note that the intensity of this absorption is much higher (at the order of (1–2) × 10^4), and unlike the visible maxima of the rest of the paraions (**3**, $R_4 \neq p\text{-}NO_2C_6H_4$) it is shifted by nonpolar solvents to a shorter wavelength (360 nm in dioxane; see Table I). An electron-donating group like *p*-methoxyphenyl (**3o–q**) located on the anionic ring causes a red shift of 14–19 nm, in agreement with previous[3] observations. ^{13}C NMR was in agreement with previous observations.[5] Spectra of two

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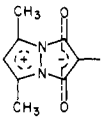
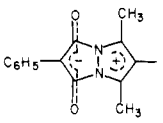
(2) Zvilichovsky, G.; Fotadar, U. *J. Org. Chem.* **1973**, *38*, 1782.
(3) Zvilichovsky, G. *Tetrahedron* **1975**, *31*, 1861.
(4) Kanemasa, S.; Potts, K. T.; Zvilichovsky, G. "Abstracts of Papers", 7th International Congress on Heterocyclic Chemistry, Tampa, FL, 1979; p 56.
(5) Potts, K. T.; Kanemasa, S.; Zvilichovsky, G. *J. Am. Chem. Soc.* **1980**, *102*, 3971 and unpublished results.
(6) Friedrichsen, W. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1980**, *35B*, 1002.
(7) The dihydroxy form is the predominant tautomer when the substituent at position 4 is aromatic as shown by IR spectra (Duban F. P.; Zinner, G. *Chem. Ber.* **1975**, *108*, 2189) and by comparison of the UV spectra with the appropriate alkyl derivatives (Zvilichovsky, G.; David, M., unpublished results).

Table I. Substituted Anhydro-1-hydroxy-3-oxopyrazolo[1,2-a]pyrazolium Hydroxides (3): Their UV-vis Spectral Data[a] and the Rate of the Anionic Ring Cleavage by Morpholine in CH_3CN at 25 °C

compd	R_1	R_2	R_3	R_4	λ_{max}, nm (ϵ, mol^{-1}) in CH_3CN [in dioxane]	dec rate const, $10^{-4}k$, s^{-1}
3a[b]	H	H	H	C_6H_5	266 (23 500), 258 (22 270),[c] 434 (1060) [445 (850)]	210
3b	CH_3	H	H	C_6H_5	267 (28 300), 259 (24 700),[c] 428 (1150) [435 (1120)]	9.1
3c[b]	CH_3	H	CH_3	C_6H_5	267 (25 300), 424 (920)	0.031
3d	C_6H_5	H	CH_3	C_6H_5	270 (37 700), 450 (530)	8.7
3e	CH_3	C_6H_5	H	C_6H_5	275 (36 440), 440 (980)	22.8
3f	C_6H_5	H	C_6H_5	C_6H_5	290 (22 500), 471 (342)	35.2
3g	CH_3	$C_6H_5CH_2$	CH_3	C_6H_5	269 (40 100), 430 (860)	0.031
3h		$-(CH_2)_4-$	CH_3	C_6H_5	270 (38 370), 432 (780)	0.021
3i		$-(CH_2)_3-$	CH_3	C_6H_5	270 (45 400), 435 (920)	
3j	H	H	H	p-$NO_2C_6H_4$	373 (21 200) [360 (22 600)]	80
3k	CH_3	H	H	p-$NO_2C_6H_4$	375 (20 070)	2.3
3l	CH_3	H	CH_3	p-$NO_2C_6H_4$	375 (11 220)	
3m[b]	H	H	H	p-ClC_6H_4	273 (28 000), 435 (1150) [443 (1160)]	79
3n	CH_3	H	CH_3	p-ClC_6H_4	276 (30 060), 421 (920)	
3o	H	H	H	p-$CH_3OC_6H_4$	267 (20 900), 259 (20 000),[c] 453 (885) [463 (950)]	220
3p	CH_3	H	H	p-$CH_3OC_6H_4$	268 (33 880), 261 (30 370),[c] 444 (1030)	12.1
3q	CH_3	H	CH_3	p-$CH_3OC_6H_4$	258 (31 380), 252 (29 680),[c] 438 (800)	0.056
6	CH_3	H	CH_3		304 (19 400), 319 (16 850), 450 (1625)	13.0
7	CH_3		CH_3	C_6H_5	270 (62 500), 283 (46 150),[c] 428 (1562)	0.41

[a] The short wavelengths (λ_{max} 200–220 nm) are not reported here. The addition of BF_3 etherate caused a reversible disappearance of the visible absorbption. For the influence of NaOH and $(C_2H_5)_3N$ see discussion in text. [b] See ref 4–6. [c] Shoulder.

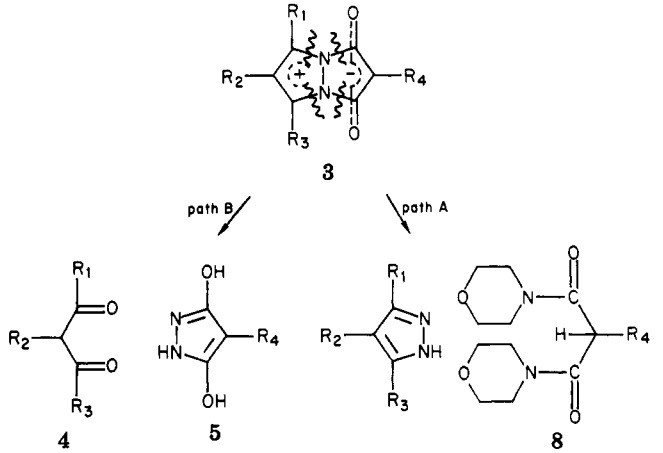
nonsymmetric derivatives (**3e** and **3d**) are given in the Experimental Section.

Interesting results were obtained by studying the influence of the paraionic moiety as a substituent linked through either the cationic or the anionic ring. The synthesis of 1,4-bis(anhydro-5,7-dimethyl-1-hydroxy-3-oxopyrazolo[1,2-*a*]pyrazol-2-ylium hydroxide)benzene (**6**) was achieved by the preparation of the bifunctional 1,4-bis(3,5-dihydroxypyrazol-4-yl)benzene, followed by treatment with acetylacetone. Compound **7**, in which the linkage is through the cationic ring, was prepared by the reaction of α-(chlorocarbonyl)ketene with 3,3′,5,5′-tetramethyl-4,4′-dipyrazole.

In compound **6** the visible absorption is shifted to longer wavelength (by 26 nm) compared to that in **3c**, as expected from an electron donating group. In compound **7** where the linkage is at position 6 there is almost no change in wavelength. However, the intensity is doubled (see Table I) as expected from the nonconjugated couple.

Stability Studies: Decomposition by Morpholine. All 19 different substituted anhydro-1-hydroxy-3-oxopyrazolo[1,2-*a*]pyrazolium hydroxide derivatives were found to be quite stable in water and in aqueous acids. They were found thermally stable at 200 °C in various organic solvents. However, they decompose under the influence of bases and amines. The decomposition by secondary amine, e.g., morpholine (Scheme III), serves as a criterion for stability. Rate constants and half-lives were determined in order to compare the various effects of substituents and conditions on the stability of the bicyclic betaines. In order to identify the products and the course of the reaction, the aminolysis was run on a large scale.

Scheme III



Kinetic studdies were carried out by following the change of light absorption in either the visible region or the UV and when necessary in both. A large excess of morpholine was used (40–1000-fold) which was enough to yield a pseudo-first-order mechanism. Pseudo-first-order rate constants which were determined are given in Tables I and II.

Effect of Solvent on the Reaction of 3 with Morpholine. Most of the kinetic measurements were taken in CH_3CN in which all derivatives of anhydrohydroxypyrazolopyrazolium hydroxide **3** were soluble enough and the reactions were fast enough to be conveniently measured. A less polar solvent, e.g., dioxane, caused a 2-fold decrease (see Table II) in the rate of cleavage of the anionic

Table II. Effect of Solvent on the Reaction of Substituted Anhydro-1-hydroxy-3-oxopyrazolo[1,2-a]pyrazolium Hydroxides (3) with Morpholine

compd	solvent	type of reaction	rate const, $10^{-4}k$, s^{-1}
3a	CH_3CN	A	210
	dioxane	A	88
	CH_3CN + 14% water	A	27
		B	49
3b	CH_3CN	A	9.1
	dioxane	A	4.5
	CH_3CN + 14% water	A	1.0
3j	CH_3CN	A	80
	dioxane	A	49
	CH_3CN + 14% water	B	1000
3m	CH_3CN	A	79
	CH_3CN + 14% water	A	14
		B	130
	dioxane + 14% water	A	15.6
		B	2.6
3o	CH_3CN	A	220
	CH_3CN + 14% water	A	32
		B	20
	dioxane	A	124

ring to form pyrazoles and the diamide 8 (cleavage A, Scheme III). The addition of water caused a decrease in the rate of the cleavage, but it brought about an increase in the rate of the cationic ring cleavage (path B, Scheme III) in cases where the latter reaction was possible (see Table II). The presence of water was essential for cleavage B; however, it did not take place without morpholine. The addition of NaOH instead of morpholine did not result in cleavage but rather in a reversible change of spectrum. This change occurred only in compounds in which the cleavage of the cationic ring with morpholine was possible. The change consisted of the disappearance of the typical visible and UV absorptions of the paraion and the formation of an intense absorption at about 350 nm ($\epsilon \sim 3 \times 10^4$) in compounds **3a**, **3m**, and **3o** and at 470 nm ($\epsilon \sim 2 \times 10^4$) in **3j**. When triethylamine was added the changes in the spectra were similar but not identical with those obtained with NaOH (370 and 450 nm, respectively). The addition of morpholine to the solution which was treated previously with triethylamine caused cleavage of the cationic pyrazole ring (path B, Scheme III). However, the addition of morpholine to solutions which were treated with NaOH did not cause any further change in their spectra.

The ratio between path A and path B (Scheme III), in solutions that contained water, was dependent on the substituents as well as on the organic solvent used. Thus the *p*-chlorophenyl derivative (**3m**) which undergoes in CH_3CN (containing 14% water) mainly a cationic ring cleavage (path B), decomposes primarily via path A when reacted with morpholine in dioxane containing the same amount of water (See Table II).

Effect of Substituents at Positions 5 and 7. Introduction of two methyl groups at positions 5 and 7 slows down rate of decomposition of the paraionic system **3**. It causes a 7000-fold decrease in the rate of cleavage of the anioic ring in CH_3CN (see Table I). One methyl group gives a 23-fold decrease in rate (compound **3b**). The large effect of methyl groups in these positions means that the 5,7-dimethyl derivative (**3c**) survives for several days while the unsubstituted compound (**3a**) under the same conditions decomposes in a few seconds. Both the 5,7-dimethyl derivative (**3c**) and the monomethyl derivative (**3b**) do not undergo cationic ring cleavage (path B). The absence of methyl groups in the cationic ring permits its cleavage by morpholine in the presence of water.

A phenyl group at position 5 has no influence on the stability; thus **3b** and **3d** have the same rate of decomposition which is 300 times faster than that with a methyl group instead of the phenyl group (**3d** and **3b** vs. **3c**; see Table I). It is assumed, therefore, that the inductive effect prevails, because in spite of the negative inductive effect of a phenyl group it has also a stabilizing resonative effect which is not manifested here. The net result is that a phenyl group does not bring about any change as compared to a hydrogen, whereas a methyl group exerts a very large rate of stability. A 5,7-diphenyl derivative (**3f**) decomposes 1150 times faster than the 5,7-dimethyl derivative (**3c**) and is only slightly more stable than the substance without substituents (**3a**).

Effet of Substituents at Position 6. The effect of substituents at this position has the same direction as those at positions **5** and **7**, but is of a much smaller magnitude. An alkyl group at position 6 as a part of a tetramethylene group bridging position 5 and 6 (compound **3h**), causes only a 1.5-fold decrease in rate of decomposition as compared to **3c**. A benzyl group at this position does not change the rate of decomposition by morpholine (compare **3g** to **3c**, Table I). A paraionic system, linked through its positive end, should be considered as an electron-attracting substituent, and as expected it exerts a destabilizing effect. Thus compound **7** decomposes 13 times faster than the compound with a hydrogen at the same position (**3c**). A phenyl group at position 6 causes destabilization; thus compound **3e** decomposes 2.5 times faster than **3b**.

Effect of Substituents at Position 2. The groups at this position were para-substituted phenyl groups. Being at the anionic end of the molecule, their expected influence is the reverse of that at the other end. An electron-donating group such as *p*-methoxyphenyl causes a small increase of the rate of decomposition of the anionic ring (path A) and a considerable decrease in the rate of path B (compare **3o–q** to **3a–c**, respectively, Tables I and II). A remarkable effect on the rate of cleavage of the anionic ring is obtained when another paraionic moiety is attached through its negative end (compound **7** compared to **3c**, Table I). The effect is much larger than with a methoxy group. This is indicative of the dual properties of the paraionic system.

Electron attracting groups such as *p*-chlorophenyl and *p*-nitrophenyl cause a decrease in the rate of cleavage A and an increase in that of path B. Compounds **3j** and **3k** undergo anionic ring cleavage 3–4 times slower than **3a** and **3b**, respectively. On the other hand compound **3j** undergoes cationic ring cleavage 20 times faster than **3a** (see Table II).

In summary it was shown that the $4n\pi$ bicyclic system which is quite stable could be prepared by a thermodynamically controlled synthesis and could be cleaved either at the anionic or at the cationic ring, depending on the substituents and the conditions. The rings are stabilized separately and what keeps them together is probably charge transfer. The latter is probably responsible for the visible light absorption. There is probably an additional stabilizing factor which is specific to paraionic compounds and deserves more attention.

Experimental Section

Melting points were taken with a Fischer-Johns apparatus and are uncorrected. Acetylacetone, 2-acetylcyclopentanone, 2-acetylcyclohexanone, benzoylacetone, malonaldehyde tetramethyl

Table III. Experimental Data of the Preparation of Substituted Anhydro-1-hydroxy-3-oxopyrazolo[1,2-a]pyrazolium Hydroxides (3) from Derivatives of 3,5-Dihydroxypyrazole and 1,3-Dicarbonyl Compounds[a]

compd	compd 4 or acetal	R_4 of 5	method	% yield	mp, °C
3a[b]	malonaldehyde tetramethyl acetal	C_6H_5	B	82	239
3b	3-oxobutyraldehyde dimethyl acetal	C_6H_5	B	62	170
3c[c]	2,4-pentanedione	C_6H_5	A	54	216
3d	1-phenyl-1,3-butanedione	C_6H_5	A	51	179
3e	3-oxo-2-phenylbutyraldehyde	C_6H_5	A	52	237
3g	3-benzyl-2,4-pentanedione	C_6H_5	A	54	203
3h	2-acetylcyclohexanone	C_6H_5	A	43	192
3i	2-acetylcyclopentanone	C_6H_5	A	40	214
3j	malonaldehyde tetramethyl acetal	p-$NO_2C_6H_4$	B	40	>300
3k	3-oxobutyraldehyde dimethyl acetal	p-$NO_2C_6H_4$	B	34	>300
3l	2,4-pentanedione	p-$NO_2C_6H_4$	A	65	>300
3m	malonaldehyde tetramethyl acetal	p-ClC_6H_4	B	33	272
3n[c]	2,4-pentanedione	p-ClC_6H_4	A	40	269
3o	malonaldehyde tetramethyl acetal	p-$CH_3OC_6H_4$	B	42	218
3p	3-oxobutyraldehyde dimethyl acetal	p-$CH_3OC_6H_4$	B	50	184
3q	2,4-pentanedione	p-$CH_3OC_6H_4$	A	44	216

[a] C, H, and N contents agreed with calculated values to within 0.3%. [b] See ref 5 and 6. [c] See ref 6.

acetal, 3-oxobutyraldehyde dimethyl acetal and ethyl α-phenylmalonate were purchased from Aldrich Chemical Co., Inc. Ethyl α-(*p*-nitro-, *p*-chloro-, and *p*-methoxyphenyl)malonates were prepared by a previously described procedure.[8] ^1H NMR spectra were determined with a Varian T-60 and ^{13}C NMR spectra with a Bruker WH-300 spectrometer. UV and visible spectra as well as kinetic studies were carried out with a Varian Techtrone spectrophotometer, Model 635. IR spectra were determined with Perkin-Elmer spectrophotometer, Model 157. If not stated otherwise, samples were dried on P_2O_5 under vacuum at 75 °C.

3,5-Dihydroxy-4-phenylpyrazole (5, R_4 = C_6H_5). Ethyl α-phenylmalonate (11.8 g) was boiled under reflux with hydrazine hydrate (15 mL) for 1 h. After the mixture cooled to room temperature, ethanol (150 mL) was added and the solution seeded with crystals of the hydrazinium salt of 3,5-dihydroxy-4-phenylpyrazole. The hydrazinium salt which precipitated [8.3 g; mp 176 °C (lit.[9] mp 176–178 °C)] was collected, redissolved in water (100 mL), and acidified with HCl to pH 1. The white precipitate was collected and recrystallized from THF: 7.2 g (overall yield 70%); mp 229 °C (lit.[9] mp 227–229 °C); UV λ_{max} (CH_3CN containing 14% water and 0.0033% morpholine) 258 nm (ϵ 16 500).

3,5-Dihydroxy-4-(*p*-nitrophenyl)pyrazole (5, R_4 = *p*-$NO_2C_6H_4$). Ethyl α-(*p*-nitrophenyl)malonate[8] (5.6 g) was boiled under reflux with hydrazine hydrate (10 mL) for 1.5 h. After the mixture cooled to room temperature, water was added (100 mL). The solution was cooled on ice and acidified with HCl to pH 1. The precipitated product was collected and recrystallized from Me_2SO–$CHCl_3$: 4.0 g (90% yield); mp >300 °C, ^1H NMR (Me_2SO-d_6) δ 8.0 (s, 4 H), 9.15 (br s, 3 exchangeable H); IR (Nujol) ν_{max} 3310 (OH, NH) cm^{-1}, no carbonyl absorption, similar to the oxygen analogue[2] UV (CH_3CN containing 14% water and 0.0033% morpholine) λ_{max} 428 nm (ϵ 13 500).

The product contained traces of Me_2SO. These were removed for purpose of analysis by dissolution in CH_3CN, precipitation of the hydrochloride salt by the addition of a few drops of HCl, filtration and resuspension in water. The solid was collected and dried in vacuum on P_2O_5 at 100 °C for 48 h.

Anal. Calcd for $C_9H_7N_3O_4$: C, 48.88; H, 3.19; N, 19.00. Found: C, 48.68; H, 3.04; N, 18.67.

3,5-Dihydroxy-4-(*p*-methoxyphenyl)pyrazole (5, R_4 = *p*-$CH_3OC_6H_4$). Ethyl α-(*p*-methoxyphenyl)malonate[8] (8.0 g) was boiled with hydrazine hydrate (3.1 mL) for 2 h, cooled to room temperature, and diluted with water (60 mL). The solution was acidified with HCl to pH 2. The product which precipitated was collected and recrystallized from dioxane: 4.8 g (77% yield); mp 225 °C; ^1H NMR (Me_2SO-d_6) δ 7–8 (q, 4 H), 9.33 (s, 3 H); IR ν_{max} 3200 cm^{-1} (OH, NH), no C=O absorption; UV (CH_3CN containing 14% water and 0.0033% morpholine) λ_{max} 264 (ϵ 18 500).

Anal. Calcd for $C_{10}H_{10}N_2O_3$: C, 58.25; H, 4.89; N, 13.59. Found: C, 58.13; H, 4.75; N, 13.36.

3,5-Dihydroxy-4-(*p*-chlorophenyl)pyrazole (5, R_4 = *p*-ClC_6H_4). This product was prepared by a procedure similar to that mentioned above for the methoxy derivative. It was obtained in 66% yield and recrystallized from DMF–ether; mp 212 °C. It absorbed at 3200 cm^{-1} (in Nujol) and had a weak absorption at 1640 cm^{-1}: ^1H NMR (Me_2SO-d_6) δ 7.7 (d, 2 H), 7.2 (d, 2 H), 9.0 (br s, 3 exchangeable H); UV (CH_3CN containing 14% water and 0.0033% morpholine) λ_{max} 285 nm (ϵ 19 850), 256 (15 000). Compound 5 did not give a satisfactory analysis; however, when it was allowed to react with dicarbonyl compounds, a series of products were obtained that gave acceptable analyses (see Table III).

Diethyl *p*-Phenylenedimalonate. Diethyl *p*-phenylenediacetate (25.2 g) was dissolved in ethyl carbonate (315 mL), and small pieces of sodium (5 g) were added. When the mixture was heated, an exothermic reaction occurred. The reaction was allowed to proceed without heating, and after it subsided the mixture was heated under reflux for 1 h. The initially formed red mixture turned light gray. After the mixture cooled, glacial acetic was added (80 mL). The solvents were evaporated under vacuum at 50 °C. A mixture of ice and water (200 g) was added, the product was extracted with ether, and the organic layer was dried on K_2CO_3, filtered, and evaporated to dryness. The yellow residue crystallized on cooling. Recrystallization from ethanol afforded the product: 19.8 g (50% yield); mp 75 °C; IR (Nujol) λ_{max} 1760 cm^{-1} (CO); ^1H NMR ($CDCl_3$) δ 7.25 (s, 4 H), 4.58 (s, 2 H), 4.35 (q, 8 H), 1.3 (t, 12 H).

Anal. Calcd for $C_{20}H_{26}O_8$: C, 60.90; H, 6.64. Found: C, 60.98; H, 6.49.

1,4-Bis(3,5-dihydroxypyrazol-4-yl)benzene. Diethyl *p*-phenylenedimalonate (3.94 g) was heated under reflux with hydrazine hydrate (10 mL) for 3 h and cooled to room temperature. Ethanol (40 mL) was added slowly. The precipitate which separated was collected, redissolved in water (60 mL), and acidified to pH 1. The product which precipitated was collected and recrystallized from Me_2SO–$CHCl_3$: 3.42 g (80% yield); mp >300 °C; IR (Nujol) ν_{max} 3160 (weak), 1620 (weak), 1585 cm^{-1} (strong); ^1H NMR (Me_2SO-d_6) δ 7.6 (s, 4 H), 9.0 (br s, 6 exchangeable H). The crystals contained two molecules of Me_2SO per molecule.

Anal. Calcd for $C_{16}H_{22}N_4O_6S_2$: C, 44.65; H, 5.15; N, 13.02; S, 14.90. Found: C, 44.65; H, 5.20; N, 13.29; S, 15.43.

3,3′,5,5′-Tetramethyl-4,4′-dipyrazole. This product was prepared from 3,4-diacetyl-2,5-hexanedione[10] and hydrazine hydrate by a known procedure;[11] mp 300 °C (lit.[11] mp 298–299 °C).

1,4-Bis(anhydro-5,7-dimethyl-1-hydroxy-3-oxopyrazolo-[1,2-*a*]pyrazol-2-ylium hydroxide)benzene (6). 1,4-Bis(3,5-dihydroxypyrazol-4-yl)benzene (0.43 g) was dissolved in DMF (2 mL). Acetylacetone (1.2 mL) was added, and the mixture boiled for 5 min. The red crystals which separated on colling were

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collected and washed with ether: 0.33 g (82% yield); mp >300 °C; IR (Nujol) ν_{max} 1670 cm^{-1} (C=O); UV and visible spectra are given in Table I.

Anal. Calcd for $C_{22}H_{18}N_4O_4$: C, 65.67; H, 4.51; N, 13.92. Found: C, 65.60; H, 4.51; N, 13.57.

6,6'-Bis(anhydro-5,7-dimethyl-1-hydroxy-3-oxo-2-phenylpyrazolo[1,2-*a*]pyrazolium hydroxide) (7). 3,3',5,5'-tetramethyl-4,4'-dipyrazole (0.19 g) was dissolved in dry THF (35 mL), and a solution of (0.4 g) α-(chlorocarbonyl)ketene[12] in dry THF (5 mL) was added with stirring at 15 °C during a 10-min period. The stirring was continued for 15 min, and the red precipitate was collected, washed with water, and recrystallized from acetic acid: 0.25 g (52% yield); mp >300 °C; UV and visible spectra are given in Table I; IR (Nujol) ν_{max} 1670 cm^{-1} (C=O).

Anal. Calcd for $C_{28}H_{22}N_4O_4$: C, 70.28; H, 4.63; N, 11.77. Found: C, 70.33; H, 4.66; N, 11.70.

Anhydro-1-hydroxy-3-oxo-2,5,7-triphenylpyrazolo[1,2-*a*]pyrazolium Hydroxide (3f). 3,5-Diphenylpyrazole[13] (1.1 g) was dissolved in dry THF (10 mL), and α-(chlorocarbonyl)ketene (1.8 g) dissolved in dry THF (4 ml) was added as in the procedure described above for **7**. The product was recrystallized from acetic acid: 0.26 g (71% yield); mp 235 °C IR (Nujol) ν_{max} 1650 cm^{-1} (C=O) UV and visible spectra are given in Table I.

Anal. Calcd for $C_{24}H_{16}N_2O_2$: C, 79.11; H, 4.43; N, 7.69. Found: C, 79.00; H, 4.22; N, 7.60.

3-Benzyl-2,4-pentanedione. This diketone, which was used for the preparation of **3g**, was prepared from acetylacetone by a known procedure.[14]

3-Oxo-2-phenylbutyraldehyde. This keto aldehyde, which was used in the preparation of **3e**, was prepared from phenylacetone by a known procedure.[15]

General Procedures for the Preparation of Anhydro-1-hydroxy-3-oxopyrazolo[1,2-*a*]pyrazolium Hydroxides (3) from Dicarbonyl Compounds. Method A. A 4-substituted 3,5-dihydroxypyrazole (**5**, 0.01 mol) was boiled with the dicarbonyl compound (4 mL) for 5 min. In the cases of the preparation of **3d,g** and **3l**, a solvent was necessary [e.g., chlorobenzene (10 mL) and DMF (2.6 mL), respectively]. In these cases the amount of the diketone was reduced to 1.1 mL. In the cases of **3n** and **3q** more of the diketone was used (10 mL). After cooling to room temperature, the mixtures were kept for 2–6 h until the colored products crystallized. The products were collected and recrystallized from acetic acid. Experiment results are summarized in Table III.

Method B. This method was used when either one or both of the carbonyl groups were blocked as methyl acetals. A 4-substituted 3,5-dihydroxypyrazole (**5**, 0.01 mol) was dissolved in THF (5 mL), and the acetal form of the dicarbonyl compound (5 mL) and HCl (2 mL) were added. In the preparation of **3j** and **3k**, DMF (15 mL) instead of THF and a larger amount of HCl (5 mL) were used. The solution was filtered and kept at room temperature for 1–2 h. In the case of **3j** and **3k** the solution was filtered after the addition of the HCl and before the addition of the dicarbonyl compound. The colored crystals which precipitated were recrystallized from acetic acid. **3j** and **3k** were crystallized from DMF. Results are summarized in Table III.

α-Phenylmalonmorpholide (8, R_4 = C_6H_5). Anhydro-1-hydroxy-3-oxo-2-phenylpyrazolo[1,2-*a*]pyrazolium hydroxide (**3a**, 2.12 g) was suspended in CH_3CN (20 mL). Morpholine (1.8 g) was added dropwise at room temperature with stirring. During the addition the color faded and the solid dissolved. The solvent was evaporated under vacuum, and ether (10 mL) was added. The solid which was formed was collected and recrystallized from 2-propanol: 1.6 g (50% yield); mp 175 °C; ^{1}H NMR ($CDCl_3$) δ 7.2 (s, 5 H), 4.9 (s, 1 H), 3.5 (br s, 8 H), 3.3 (br s, 8 H); IR (Nujol) ν_{max} 1640 cm^{-1} (C=O); UV (CH_3CN containing 0.0033% morpholine) λ_{max} 315 nm (ε 860). The etheral solution from which the amide precipitated contained more of the amide and pyrazole.

Anal. Calcd for $C_{17}H_{22}N_2O_4$: C, 64.13; H, 6.97; N, 8.80. Found: C, 64.20; H, 6.65; N, 8.91.

α-(*p*-Methoxyphenyl)malonmorpholide (8, R_4 = *p*-$CH_3OC_6H_4$). Compound **3o** (2.42 g) was treated with morpholine as for **3a** above, resulting in the amide: 1.9 g (55% yield); mp 151 °C; ^{1}H NMR ($CDCl_3$) δ 7.01 (s, 4 H), 4.9 (s, 1 H) 3.8 (s, 3 H), 3.2–3.75 (br s, 16 H); IR (Nujol) ν_{max} 1670 cm^{-1} (C=O); UV (CH_3CN containing 0.0033% morpholine) λ_{max} 276 nm (ε 1400), 283 (1200).

Anal. Calcd for $C_{18}H_{24}N_2O_5$: C, 62.05; H, 6.94; N, 8.04. Found: C, 62.00; H, 6.71; N, 8.00.

Kinetic Studies of Decomposition of Substituted Anhydro-1-hydroxy-3-oxopyrazolo[1,2-*a*]pyrazolium Hydroxide (3). The concentration of the substrate in CH_3CN for studies in the visible and UV ranges were 1×10^{-3} and 4×10^{-5} M, respectively. All measurements were taken at 25 °C. For compounds that decomposed fast ($t_{1/2}$ = 0.1–30 min) scanning at a certain wavelength started right after the addition of morpholine in CH_3CN (0.1 mL, 1:10) into 3.0 mL of the solution in a quartz cell. Where rates were slow ($t_{1/2}$ = 4–100 h), the whole spectrum was taken at intervals.

The rate constants (k) were derived from both the half-lives and the slope of ln C_s vs. time, where C_s is the concentration of the substrate (the starting paraion). In cases where the k was derived from following the formation of a decomposition product, it was derived from the slope of ln ($C_o - C_p$) vs. time, where C_o and C_p are the initial concentration of the starting material and the concentration of the product, respectively. When parallel reactions were studied, the various rate constants could be derived from the equations[16] $k_A + k_B = k$ and $k_A/k_B = C_{PA}/C_{PB}$, where C_{PA} and C_{PB} are the concentrations of products of the anionic and cationic cleavage, respectively. All constants were of pseudo first order. Identification of products was accomplished by spectral comparison with authentic samples.

^{13}C NMR of Anhydro-2,6-diphenyl-1-hydroxy-5-methyl-3-oxopyrazolo[1,2-*a*]pyrazolium Hydroxide (3e) in Me_2SO-d_6: 159.4, 157.5 ($C_{1,3}$) 150.4, 141.5 ($C_{5,7}$), 132.6–123.85 (2Ph + C_6), 80.5 (C_2), 10.4 ppm (CH_3).

^{13}C NMR of Anhydro-2,5-diphenyl-1-hydroxy-7-methyl-3-oxopyrazolo[1,2-*a*]pyrazolium Hydroxide (3d) in Me_2SO-d_6: 159.3, 158.7 ($C_{1,3}$) 146.1, 144.8 ($C_{5,7}$), 133.1–123.9 (2Ph), 112.4 (C_6), 81.5 (C_2), 11.5 (CH_3).

Registry No. 3a, 75526-82-8; **3b**, 79815-52-4; **3c**, 76434-58-7; **3d**, 79815-53-5; **3e**, 79815-54-6; **3f**, 79815-55-7; **3g**, 79815-56-8; **3h**, 79815-57-9; **3i**, 79815-58-0; **3j**, 79815-59-1; **3k**, 79815-60-4; **3l**, 79815-61-5; **3m**, 79815-62-6; **3n**, 76426-56-7; **3o**, 79815-63-7; **3p**, 79815-64-8; **3q**, 79815-65-9; **4** (R_1 = R_2 = R_3 = H), 542-78-9; **4** (R_1 = Me; R_2 = R_3 = H), 625-34-3; **4** (R_1 = Me; R_2 = H; R_3 = Me), 123-54-6; **4** (R_1 = Ph; R_2 = H; R_3 = Me), 93-91-4; **4** (R_1 = Me; R_2 = Ph; R_3 = H), 63726-68-1; **4** (R_1 = Ph; R_2 = H; R_3 = Ph), 120-46-7; **4** (R_1 = Me; R_2 = CH_2Ph; R_3 = Me), 1134-87-8; **4** (R_1, R_2 = $(CH_2)_4$; R_3 = Me), 874-23-7; **4** (R_1, R_2 = $(CH_2)_3$; R_3 = Me), 1670-46-8; **5** (R_4 = Ph), 23876-79-1; **5** (R_4 = *p*-C_6H_4-NO_2), 79815-66-0; **5** (R_4 = *p*-C_6H_4-Cl), 79815-67-1; **5** (R_4 = *p*-C_6H_4-O-Me), 79815-68-2; **6**, 79815-69-3; **7**, 79815-70-6; **8** (R_4 = Ph), 79815-71-7; **8** (R_4 = *p*-C_6H_4-O-Me), 79815-72-8; ethyl hydrogen-*p*-phenylenedimalonate, 79815-73-9; 1,4-bis(3,5-dihydroxypyrazol-4-yl)benzene, 79815-74-0; 3,3',5,5'-tetramethyl-4,4'-dipyrazole, 4054-67-5; 3,5-diphenylpyrazole, 1145-01-3.

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