factory system for crystallizing the compound in high yield could not be found. Some crystalline material could be obtained from a hexane–petroleum ether (bp 30–60 °C) mixture, but the remainder separated as an oil. The bright yellow crystalline material melted sharply at 50 °C and turned red on exposure to light: IR (CCl_4) 1622, 1585, 1522, 1488, 1342, 831, 699 cm^{-1}; NMR ($CDCl_3$) δ 2.42 (s, 3 H), 7.07–8.07 (m, 8 H), 8.85 (s, 1 H). Anal. Calcd for $C_{14}H_{12}N_2O_2$: C, 69.99; H, 5.03; N, 11.66. Found: C, 70.05; H, 5.09; N, 11.41.

5-Methyl-2-phenyl-2*H*-indazole (2). A mixture of 2.60 g (10.8 mmol) of **5** in 6 mL (6.2 g, 37 mmol) of triethyl phosphite (Eastman pract) was refluxed under nitrogen for 6 h.[17] Vacuum distillation of the excess triethyl phosphite left a black residue which was chromatographed on Brockman activity 1 neutral alumina (Baker) with 4:1 benzene–chloroform as the eluent. The indazole was contained in the first 25 mL of eluent and was isolated by evaporating the solvent and crystallizing the residue from methanol–water. The yield after two crystallizations was 28%; mp 110–111 °C.

Acknowledgment. The authors are indebted to the National Science Foundation and the Lafayette College Research Fund for support of this research.

Registry No. 1, 72867-26-6; **2**, 72867-27-7; **3**, 66424-92-8; **4**, 5858-28-6; **5**, 72867-28-8; 4-(dichloromethyl)-4-methyl-2,5-cyclohexadien-1-one, 6611-78-5; aniline, 62-53-3.

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[17] J. I. G. Cadogen et al., *J. Chem. Soc.*, 4831 (1965).

N-Methyl-1,2,3,4-tetrahydropyridine

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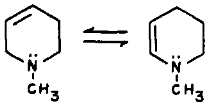
Received November 8, 1979

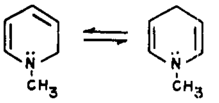
It has long been recognized that the lone pair of electrons on nitrogen interacts with an adjacent double bond. This is a very strong interaction, and this arrangement of substituents behaves as a single functional group.[1]

In spite of interest in enamines from both a theoretical and synthetic point of view, they have not been studied as extensively as dienes. For example, the enamines that have attracted the most attention have been prepared from carbonyl compounds and secondary amines such as pyrrolidine, piperidine, and morpholine.[1]

The simple enamine **2**, *N*-methyl-1,2,3,4-tetrahydropyridine, is electronically analogous to cyclohexa-1,3-diene. Because the nitrogen atom and double bond are part of the same ring in enamine **2**, molecular models indicate that the interaction between the lone pair of electrons on nitrogen and the π molecular orbitals of the double bond should be large. In spite of the interest in this simple enamine, previous attempts to prepare **2** have been unsuccessful.[2]



1 2

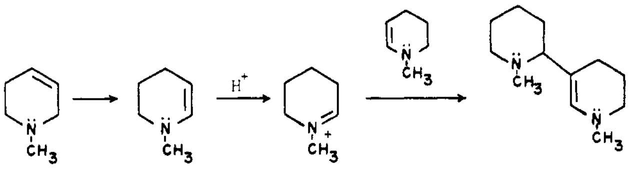


3 4

In connection with our earlier work on the base-catalyzed equilibration of the dihydropyridines **3** and **4**[3] we also studied the base-catalyzed equilibration of the allylamine **1** and the enamine **2**. The recent publication by Martinez and Joule[2b] on the base-catalyzed isomerization of **1** has prompted us to report our results on this system.

We have observed that the enamine **2** can be prepared by the treatment of allyl amine **1** with 1.0 M potassium *tert*-butoxide in dimethyl sulfoxide. If this isomerization is carried out in a 5-mm NMR tube, it can be followed by ^1H NMR spectroscopy by observing the appearance of the characteristic enamine vinyl hydrogens of **2**. The pure enamine **2** can be isolated by the addition of water to the reaction mixture, followed by extraction with pentane. However, the enamine **2** is extremely unstable and care must be exercised in this workup procedure (see the Experimental Section). The enamine **2** is stable if stored in the refrigerator (5 °C) over potassium hydroxide pellets.

Martinez and Joule[2b] also concluded that the allyl amine **1** is isomerized to the vinyl amine **2** by potassium *tert*-butoxide in dimethyl sulfoxide. However, they were unable to directly observe or isolate the vinyl amine **2**. The main product they isolated from their base-catalyzed isomerizations was *N*,*N*′-dimethyl-1,4,5,6-tetrahydroanabasine.[5]



1 2 5

Since **5** is undoubtedly produced from the dimerization of **2**, they inferred that potassium *tert*-butoxide in dimethyl sulfoxide catalyzes the isomerization of **1** to **2**. From their data they concluded that the dimerization occurs in the presence of the strong base and not in the workup procedure. This is probably not the case since under almost identical conditions we can directly observe the enamine **2** by proton magnetic resonance and we can isolate the enamine **2** if care is taken in the workup procedure.

The dihydropyridines **3** and **4** both contain the enamine function and, in principle, are capable of undergoing an acid-catalyzed dimerization analagous to that observed for **2**. We have observed qualitatively that the relative stability of these enamines with respect to dimerization in glass storage vessels is **4** > **3** > **2**. Enamine **2** is by far the most reactive. It undergoes dimerization within minutes in the absence of potassium hydroxide pellets, whereas **3** is stable for days and **4** is stable for weeks under similar conditions.

The enamine **2** is clearly more unstable with respect to acid-catalyzed dimerization than most aldimines.[1] This instability suggests that for enamine **2** there is a strong π interaction between the nitrogen lone pair of electrons and the carbon–carbon double bond. This interaction would stabilize the transition state involving electrophilic attack on the enamine double bond.

Since the treatment of **1** with potassium *tert*-butoxide in dimethyl sulfoxide results in equilibration of **1** and **2**, a measurement of the equilibrium constant of this system would allow for an estimation of enamine stabilization. Although it is generally accepted that enamines are more stable than the allyl amines there are few examples of a direct measurement of the equilibrium constant.[1,2b] We

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[1] Cook, A. G. "Enamines: Synthesis, Structure and Reactions"; Marcel Dekker: New York, 1969.

[2] (a) Leonard, N. J.; Hauck, F. P. *J. Am. Chem. Soc.* **1957**, *79*, 5279. (b) Martinez, S. J.; Joule, J. A. *Tetrahedron* **1978**, *34*, 3027.

[3] Fowler, F. W. *J. Am. Chem. Soc.* **1972**, *94*, 5926.

[4] Bates, R. B.; Carrighan, R. H.; and Staples, C. E. *J. Am. Chem. Soc.* **1963**, *85*, 3031.

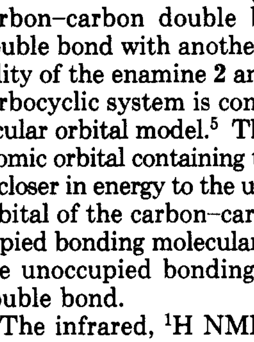
[5] Libit, L.; Hoffmann, R. *J. Am. Chem. Soc.* **1974**, *96*, 1370.

0022-3263/80/1945-1336$01.00/0

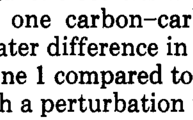
have analyzed the reaction mixture produced when 1 is treated with 1.0 M potassium *tert*-butoxide in dimethyl sulfoxide by gas–liquid chromatography. From the relative quantities of 1 and 2 present at 91.6 °C after equilibration, the free-energy difference between these compounds was calculated to be 4.0 kcal/mol. Direct observation by proton and carbon-13 magnetic resonance of the reaction mixture after base treatment does not show the presence of the allyl amine 1 and confirms that this equilibrium strongly favors amine 2. Unfortunately, there is no independent synthesis of 2 and the equilibrium can only be approached from one direction. Although we are confident that equilibrium was established, the free-energy difference of 4.0 kcal/mol should be considered to be a lower limit. That is, the free-energy difference between 1 and 2 is probably at least 4.0 kcal/mol.

In contrast to the heterocycle 2 and its unconjugated isomer 1, cyclohexa-1,3-diene is only 0.07 kcal/mol more stable than its unconjugated isomer, cyclohexa-1,4-diene.[4] This observation suggests that greater stability results from the interaction of a nitrogen lone pair of electrons with a carbon–carbon double bond than one carbon–carbon double bond with another. The greater difference in stability of the enamine 2 and allyl amine 1 compared to the carbocyclic system is consistent with a perturbation molecular orbital model.[5] The energy difference between the atomic orbital containing the nitrogen lone pair of electrons is closer in energy to the unoccupied antibonding molecular orbital of the carbon–carbon double bond than is the occupied bonding molecular orbital of one double bond with the unoccupied bonding molecular orbital of the other double bond.

The infrared, ^{1}H NMR, and ^{13}C NMR spectra of enamine 2 are typical (see Experimental Section) of an enamine. However, the photoelectron spectrum of 2 shows some interesting features. The first two ionization bands occur at 7.57 and 10.40 eV. These can be assigned primarily to the nitrogen lone pair of electrons (n_N) and the carbon–carbon double bond (π). The large separation of these two bands (ΔE = 2.83 eV) suggests a very strong π interaction between the lone pair of electrons on nitrogen and the double bond. This value is larger than that for simple enamines.[6] It is considerably larger than the n_N and π interaction (ΔE = 0.97 eV) of dehydroquinuclidine (6). The configuration of 6 prohibits a π interaction between the nitrogen lone pair and carbon–carbon double bond.[6a] In contrast to 6 molecular models indicate the most stable conformation of 2 has a favorable arrangement for a π interaction between the nitrogen lone pair and the carbon–carbon double bond.[7]



2



6

In summary, we have prepared *N*-methyl-1,2,3,4-tetrahydropyridine. It is a kinetically unstable enamine with respect to dimerization. However, it is a thermodynamically stable enamine with respect to the isomeric allyl amine, and the free-energy difference observed between 1 and 2 (4.0 kcal/mol) is somewhat larger than the value (2.5 kcal/mol) Martinez and Joule suggest for allyl amines and enamines.[2b] The photoelectron spectrum shows an unusually large splitting of the n and π orbitals.

All of the above data are consistent with a large interaction between the nitrogen lone pair of electrons and the double bond. The strong interaction in enamine 2 compared to other enamines studied is probably due to the presence of both the nitrogen atom and carbon–carbon double bond in the same six-membered ring. Rotation about the carbon–nitrogen bond of the enamine is not possible, and the most stable conformer of enamine 2 would maximize the π interaction of the nitrogen lone pair of electrons and the double bond.

Experimental Section

The proton magnetic resonance spectra (^{1}H NMR) were recorded with a Varian EM-360 or HFT-80 spectrometer. Apparent coupling constants are reported and the multiplicities are indicated by using s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. The carbon-13 magnetic resonance spectra (^{13}C NMR) were recorded with a Varian CFT-20 spectrometer. Chemical shifts for both the ^{13}C and ^{1}H NMR spectra are reported as δ values in parts per million from tetramethylsilane as an internal standard. The infrared spectra were recorded with a Perkin-Elmer 727 or 567 spectrometer. The relative intensities are indicated by s = strong, m = medium, and w = weak. The photoelectron spectra were recorded on a Perkin-Elmer PS-18 spectrometer with a He(I) source using xenon and argon calibration standards. Vertical ionization potentials were reported and are accurate to 0.05 eV.

***N*-Methyl-1,2,3,4-tetrahydropyridine (2).** To a tube containing 10 mL of 1.0 M potassium *tert*-butoxide in dimethyl sulfoxide was added 4.55 g of the amine 1.[8] The tube was flushed with N_2 and sealed under vacuum. The reaction mixture was heated to 91.6 °C for 2 days. At the end of this time an equal volume of water was added and the reaction was rapidly extracted three times with pentane. The pentane extracts were combined, washed with water, and dried with KOH. The pentane was removed in a stream of nitrogen and the residue was bulb-to-bulb distilled to give 2.30 g of a clear liquid: ^{1}H NMR (benzene-d_6, HFT-80) 1.50–2.05 (m, 4 H), 2.27 (s, 3 H), 2.45–2.70 (m, 2 H), 4.35–4.60 (m, 1 H), and 5.72 (d of t, J = 7.9, 1.6, 1 H); IR (film) 3050 (m), 2940 (s), 1642 (s), 1445 (m), 1400 (m), 1319 (s), 1190 (s), 1048 (s), and 700 cm^{-1} (m); ^{13}C NMR (benzene-d_6) 137.6, 97.3, 50.0, 42.8, 23.2, and 21.4.

Equilibration of 1 and 2. The amine 1 was purified by GLC (85 °C, 5 ft × 0.25 in. 10% Carbowax on Chrom W column). The 1.0 M potassium *tert*-butoxide in dimethyl sulfoxide was prepared from dimethyl sulfoxide, freshly distilled from CaH_2 and sublimed potassium *tert*-butoxide. To Pyrex tubes equipped with a rubber septum that had previously been washed with 28% NH_3, dried at ca. 150 °C, and flushed with N_2 was added a known quantity (ca. 0.2 g) of amine 1, 0.400 mL of 1.0 M potassium *tert*-butoxide, and a known quantity (ca. 0.002 g) of *N*-methylpiperidine as an internal standard. The tubes were frozen, evacuated, flushed with N_2 several times, and sealed. They were then placed in a constant temperature bath (91.6 °C) for ca. 2 days. The ratio of 1 to 2 did not change appreciably by running the reaction for a longer period of time. This time is estimated to be approximately 12 half-lives, following the rate of the reaction by ^{1}H NMR spectroscopy. Analysis of the product mixture was performed with a 5 ft × 0.25 in. 10% Carbowax on Chrom W column at 62 °C. The amine 1 and *N*-methylpiperidine had retention times of 3.06 and 2.38 min, respectively. The equilibrium constant was determined by measuring the ratio of amine 1 to *N*-methylpiperidine. Because

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[6] (a) Brown, R. S. *Can. J. Chem.* **1976**, *54*, 1521. (b) Domelsmith, L. N.; Houck, K. N. *Tetrahedron Lett.* **1977**, 1981. (c) Sustmann, R.; Trill, H. *Angew. Chem., Int. Ed., Engl.* **1972**, *11*, 838. Itoh, T.; Kaneda, K.; Watanabe, I.; Ikeda, S.; Teranishi, S. *Chem. Lett.* **1976**, 227.

[7] The most stable conformation of 2 was assumed to be the half-chair. This conformation minimizes adjacent nonbonded hydrogen–hydrogen interactions and is analogous to the most stable conformation of cyclohexene (see Allinger, N. L.; Sprague, J. T. *J. Am. Chem. Soc.* **1972**, *94*, 5734 and references cited therein).

[8] Aldrich Chemical Co., 940 West Saint Paul Ave., Milwaukee, WI 53233.

of the reactivity of the enamine 2 it completely decomposed on the GLC column and could not be measured directly. The free-energy difference between 1 and 2 at 91.6 °C, calculated from three runs containing three samples each, was 4.0 ± 0.1 kcal/mol.

Acknowledgment is made to the National Science Foundation for financial support (CHE 7807517).

Registry No. 1, 694-55-3; 2, 57005-69-3.

Pseudooxocarbons. Synthesis of 1,2,3-Tris(dicyanomethylene)croconate Salts. A New Bond-Delocalized Dianion, Croconate Blue[1]

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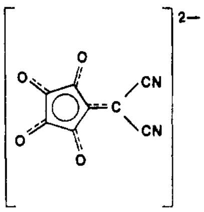
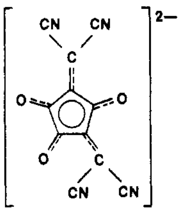
Received December 13, 1979

In a recent paper,[2,3] the synthesis and characterization of 2-(dicyanomethylene)- and 1,3-bis(dicyanomethylene)croconate salts, 1 and 2 (dipotassium salts), respectively, have been reported. The bond-delocalized dianions 1 and 2 are new additions to the aromatic oxocarbons[4] $(C_nO_n)^{m-}$. Here, the preparation and some of the properties of the croconate dianion analogue in which three of the carbonyl oxygen atoms are replaced by dicyanomethylene groups, e.g., the dianion 3 (dipotassium salt), are described.



1



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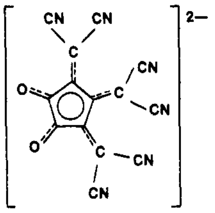
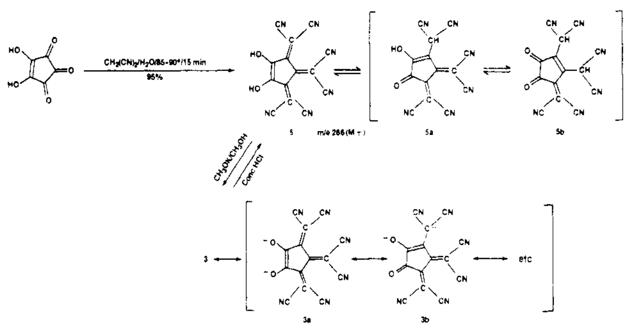


3

When a mixture of croconic acid (4) (4,5-dihydroxy-4-cyclopentene-1,2,3-trione) and malononitrile in water was briefly heated at 85-90 °C, a new oxocyanocarbon acid 5 was isolated in over 90 percent yield (Scheme I). It was termed "croconic acid blue" because of its intense blue color in water: UV (H_2O) 600 nm (ε 55 000). The acid 5 is an intensely solvatochromic dye, the color of which is dependent on the polarity of the solvent; for example, its solution in anhydrous acetone (or ethyl alcohol) is red [UV (Me_2CO) 475-480 nm], but in water it is deep blue. The IR (KBr) of the acid 5 shows bands at 1755 (s), 1700 (sh, C=O), 1650 (s), 1590 (s), and 1520 cm^{-1} [s, C=O, C=C, C=C(CN)$_2$], indicating the possible existence of tautomers with C-H structures **5a** ⇄ **5b** in the solid. The acid 5 is a strong oxocyanocarbon acid[5] (p$K_2 \approx 1$); it is stronger than croconic acid but weaker than croconic acid violet (the conjugate of 2). In water at room temperature, acid 5 hydrolyzes slowly (95% in 85 days) to yield the more thermodynamically stable croconic acid violet [UV (H_2O) 533 nm]. However, excessive heating of 5 in water causes apparent polymerization, to afford deep green, lustrous plates [UV (H_2O) 590-595 (sh), 535, 510, and 490 nm]; it showed no molecular-ion peak in its mass spectrum.

Scheme I



Acid 5 was readily converted into the green-blue dipotassium salt of 1,2,3-tris(dicyanomethylene)-4-cyclopentene-4,5-diol, e.g., 3, on careful titration with potassium methoxide in methanol. Similarly, bis(tetramethylammonium) or pyridinium[6] salts of 3 were prepared.

The dipotassium salt of 3 is a dye,[7] named "croconate blue" because of its intense, blue color in solution; the electronic spectrum of the dianion 3 in aqueous solution shows a band at 599 nm (ε 54 600). It should be noted that the acid 5 and the salt of 3 absorb in the same region, with almost the same intensity in the visible spectrum (ε 54 600 vs. 55 000). The infrared spectrum of the dipotassium salt of 3 shows bands at 1670 (s, C=O), 1620 (s), and 1570 cm^{-1} [m, C=O, C=C, C=C(CN)$_2$], indicating possible contributions from the resonance forms **3a** ↔ **3b** ↔ etc. Indeed, the highly absorbing salt gave a Raman spectrum (λ_0 514.5 nm, Figure 1; see Experimental Section) showing a strong fluorescence at 900 cm^{-1}. The Raman spectrum of 3 (Figure 1) shows bands at 2208 (s, C≡N), 1654 (m, C=O), 1596 (m), 1572 (m), 1551 [s, C=O, C=C, C=C(CN)$_2$], and 1472 cm^{-1} (m, dianion), also indicating possible contributions from the resonance forms **3a** ↔ **3b** ↔ etc. The ^{13}C NMR spectrum (Experimental Section) of 3 resembled that of the acid 5, which supports the symmetrical structure of the dianion 3 and the dianion 5 formed by ionization. Cyclic voltammetry of the salt (in water, 0.1 M sodium perchlorate as the supporting electrolyte, mercury electrode, concentration 240 mM, scan rate of 50 mV s^{-1} vs. SCE) and DC polarography revealed a stepwise reduction by a two-electron-transfer mechanism, as shown by three irreversible peak potentials at −0.69, −0.93, and −1.15 V [e.g., $2C{=}C(CN)_2 \rightarrow (NC)_2CHC{=}CCH(CN)_2$]. The first reduction wave of the dipotassium salt of 3 at −0.69 V vs. SCE indicates that 3 is easier to reduce than the dipotassium salt of 2 ($E_{1/2}$ = −0.88 V vs. SCE) and more difficult than dilithium croconate ($E_{1/2}$ = −0.48 V vs. SCE).

The high acidity of the oxocyanocarbon acid 5 is typical of the symmetrical, bond-delocalized structure of its dianion 3 (as also observed for the dianions 1 and 2 and their conjugate acids). However, a stereomodel of the crowded dianion 3 (the van der Waals contacts between two neighboring nitrogen atoms are less than 3 Å) indicates that to relieve the steric hindrance of the 1,2,3-tris(dicyanomethylene) groups a staggered conformation of all of the cyano groups in 3 is required; the estimated twist

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[1] A. J. Fatiadi, Abstracts, 178th National Meeting of the American Chemical Society, Washington, DC, Sept 9-14, 1979, No. ORGN 120.

[2] A. J. Fatiadi, *J. Am. Chem. Soc.*, **100**, 2586 (1978).

[3] A. J. Fatiadi, *Synthesis*, **165**, 240 (1978).

[4] R. West and J. Niu, "Nonbenzenoid Aromatics", Vol. 1, J. P. Snyder, Ed., Academic Press, New York, 1969, Chapter 6; "The Chemistry of the Carbonyl Group", Vol. 2, J. Zabicky, Ed., Interscience, New York, 1970, Chapter 4.

[5] L. M. Schwartz, personal communication.

[6] All new compounds gave satisfactory elemental analyses.

[7] Aqueous or alcoholic solutions of 3 (acid or salt) impart adherent stains to the skin; consequently, all operations require the use of rubber or plastic gloves.