(containing 90 to 95% COFCl) was required, since the presence of $COCl_2$ and $COF_2$ as impurities did not result in the formation of undesired products provided COFCl was used in excess. All the other chemicals were purchased from supply houses.

**Preparation of Substituted Phenyl Fluoroformates.**—All reactions were carried out in the same way, except for slight variations in reaction time, temperature, solvent, and amount of reactants (listed in Table I). In a typical experiment, *p*-fluorophenol (0.1 mole), COFCl (0.3 mole), toluene (50 m.) as a solvent, and tributylamine (0.5 ml.) as a catalyst were placed into a 150-ml. stainless steel lecture bottle equipped with a pressure gauge and a Whitey valve. The lecture bottle was agitated 16 hr. at 60° (external heating by two infrared lamps). The volatile products, mostly HCl and excess carbonyl halides, were bled off. The product was degassed at room temperature in a vacuum. The resulting solution was filtered and vacuum distilled. The conversion of the starting material and yield of *p*-fluorophenyl fluoroformate were determined by the g.c. ratios of the crude product before distillation and are listed in Table I. The yields after distillation were usually somewhat lower due to mechanical losses during the distillation. Physical and spectral properties of the substituted phenyl fluoroformates are listed in Table II.

**Decarboxylation of the Substituted Phenyl Fluoroformates.**—The same setup was used for all reactions. A stream of dry $N_2$, monitored by a flowmeter, was passed through a 10-ml. flask, containing the fluoroformate starting material. A fluoroformate vapor pressure of 100 mm. was maintained by external heating of the flask with an oil bath. The fluoroformate–nitrogen mixture was passed through an electrically heated quartz tube with Pt gauze used as filling. The products were quenched at the exit of the tube by two cold traps, one at −78 and the other at −196°. The second trap was connected to a mercury blowoff. The heating of the reaction tube was automatically controlled and its temperature was measured with a thermocouple on its outside wall. The inlet part of the setup between the fluoroformate container and the reaction tube was heated by three infrared lamps to prevent condensation of the starting material. The conversion of the starting material and the yields were determined by weighing of the recovered starting material and of the collected products. The composition of the products was analyzed by g.c. The compounds themselves were identified after g.c. separation by infrared measurements and by n.m.r. measurements. The results of all these reactions are summarized in Table III.

# Thermochromic Compounds. II

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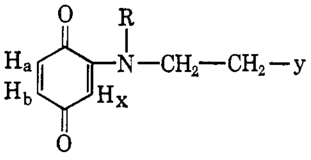
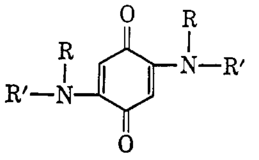
*Received June 9, 1965*

$\beta$-Hydroxyl secondary amines react with quinones to form monosubstituted compounds which are thermochromic. N.m.r. spectra show that the structure of the "colorless" thermochromic compound is not I, but a product formed from I by intramolecular reaction between the hydroxyl group and the quinone moiety.

Konig and co-workers[2-4] have reported that certain compounds of type I (Y = OH) are thermochromic,[5] piezochromic, solvatochromic, fluorescent, soluble in base as well as in acid, and have an unusual double polarographic reduction curve.



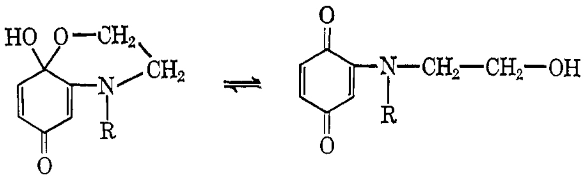


Ia, R = $CH_2CH_2OH$; Y = OH
b, R = $CH_3$; Y = OH
c, R = $CH_3$; Y = Cl

IIa, R = H; R′ = $CH_2CH_2OH$
b, NRR′ = morpholinyl

These properties are related to specific structural details: the hydroxyl group must be on the carbon $\beta$ to the nitrogen, the R group may not be a hydrogen, the hydrogen $\alpha$ to the nitrogen may not be substituted, and the quinone ring may be substituted at $H_a$ and $H_b$ with methyl groups or a fused ring. Similar compounds lacking any one of these structural details show none of the above listed properties. The 2,5-disubstituted $\beta$-ethanolaminoquinones are not thermochromic.

The nonthermochromic aminoquinones are deeply colored, while the thermochromic quinones are light in color but become deeply colored when their solutions are heated. A temperature-dependent equilibrium has been suggested for the thermochromic mechanism.[4]



cold form
III

hot form
IV

There are several reasonable structures and equilibria which might be proposed. For this reason the n.m.r. spectra of three of these compounds and several model compounds were run at temperatures from 37 to 120° to determine the structure and equilibrium responsible for the thermochromism and other unusual properties.

## Results

The spectrum of Ic is relatively simple, as seen in Table I. The spectrum showed no temperature dependence.

Table I

Absorption Peaks of Compound Ic at 37°

| In $CDCl_3$ | | In DMSO-$d_6$ | | No. of protons | Assignment | Ref.[a] |
|---|---|---|---|---|---|---|
| P.p.m. | Shape | P.p.m. | Shape | | | |
| 6.66 | 2 peaks | 6.76 | 2 peaks | 2 | Ring | 314 |
| 5.71 | Singlet | 5.70 | Singlet | 1 | Ring | |
| 3.81 | Quartet | 3.95 | Triplet | 4 | Methylenes | 12, 29, 31, 199 |
| 3.10 | Sharp | 3.10 | Sharp | 3 | Methyl | 91, 610 |

[a] The numbers given are the spectra numbers from "NMR Spectra Catalog," N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, Ed., Varian Associates, Inc., Palo Alto, Calif., 1962.

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[1] Summer N.S.F. Teacher Research Participation Program, Dominican College, Racine, Wis.

[2] K.-H. Konig, *Chem. Ber.*, **92**, 257 (1959).

[3] K.-H. Konig and G. Letsch, *ibid.*, **92**, 1789 (1959).

[4] H. Berg, K.-H. Konig, D. Tresselt, and H. Wagner, "Contributi Teorici e Sperimentali di Polarografia," Vol. 5, Consiglio Nazionale Delle Ricerche, Spoleto, Italy, 1960.

[5] J. H. Day, *Chem. Rev.*, **63**, 65 (1963).

Replacement of the chlorine by hydroxyl greatly changes and complicates the spectrum. It is convenient to discuss the spectra in terms of three separate regions: the ring protons, the hydroxyl protons, and the methylene protons.

The three ring protons of Ia and Ib, identifiable by their downfield positions and integrated intensity, give a well defined ABX spectrum, which is unaffected by change in temperature or by the addition of deuterium oxide. Numerical data are given in Table II. The six-line AB portion with a doublet X portion has been noted before.[6] This spectrum matches the theoretical spectrum in number, position, and relative intensities for an ABX spectrum as calculated by the 1620 IBM computer: $J_{AB} = 10.0$ c.p.s., $J_{BX} = 1.8$ c.p.s., $J_{AX} = 0$ c.p.s.

TABLE II

ABSORPTION PEAKS OF THE RING PROTONS[a]

| Proton | Ic | Ib | Ia | Calcd. for Ia |
|---|---|---|---|---|
| $H_a$ | 6.76 | 6.55 | 6.47 | 6.44 |
| | | 6.37 | 6.30 | 6.31 |
| $H_b$ | 6.76 | 5.95 | 5.84 | 5.80 |
| | | 5.91 | 5.80 | 5.76 |
| | | 5.78 | 5.66 | 5.64 |
| | | 5.75 | 5.63 | 5.61 |
| $H_x$ | 5.70 | 5.03 | 5.02 | 5.01 |
| | | 5.00 | 4.98 | 4.98 |

[a] Given in parts per million. Spectrum was measured in DMSO-$d_6$.

From Table II it is apparent that replacing the chlorine with a hydroxyl affects the ring in such a way as to render the $H_a$ and $H_b$ protons nonequivalent, and to decrease slightly the degree of conjugation of the ring itself, without removing any protons from the ring. In both the thermochromic Ia and Ib there is a broad peak at 7.14 p.p.m., which moves upfield 0.4 c.p.s./deg. as temperature is raised. This peak diminishes in intensity with increasing temperature, vanishing entirely near 100°.

A typical ethanolic triplet, which integrates to one proton, appears at 4.77 p.p.m. for compound Ia only; it moves upfield and flattens with increasing temperature, but does not decrease in integrated intensity. (Figure 1). Addition of deuterium oxide to solutions of Ia and Ib removes both the 7.14 (7.28 in Ib) and 4.77 peaks, confirming their identity as active hydrogens. IIa has a normal primary alcohol triplet centered at 4.73 p.p.m., with no active hydrogen further downfield. Thus, an ethanolic group behaves normally in the nonthermochromic compounds, and the lack of such a group in Ib (and lack of a second ethanolic group in Ia) demonstrates that the expected ethanolic group does not exist in the thermochromic compounds.

The low-field active hydrogen peak of Ib is present in $CDCl_3$ solution and hence is a property of the molecule rather than a solvent-induced peak. In pyridine-$d_5$ the Ib spectrum is essentially the same as in DMSO-$d_6$ except for a sharpening of the methylene region, and the low-field proton is masked by the pyridine. Temperature behavior in pyridine parallels that in DMSO-$d_6$.

The methyl peak at 2.88 p.p.m. for compound Ib is a sharp singlet, undisturbed by temperature changes; it was used as a reference for integrations.

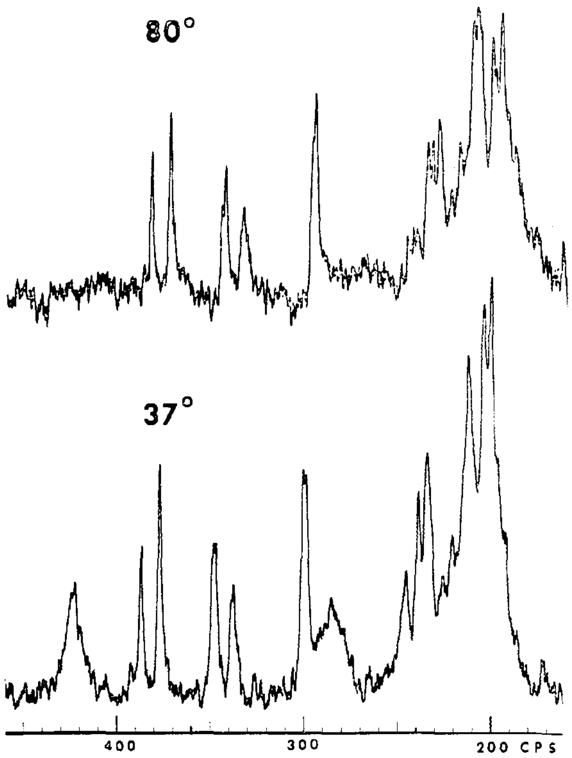

Figure 1.—N.m.r. spectrum of Ia.

IIa (Figure 2) and IIb were run to provide model spectra for comparisons. IIa shows exactly the spectrum expected; a wide N–H peak at 7.37 p.p.m., a sharp peak for the two ring protons at 5.25, a primary alcohol triplet centered at 4.73, and a methylene region of two triplets covering the region from 3.60 to 3.15. IIb was so insoluble that only a weak spectrum could be obtained, which showed two regions of absorption for the methylene protons at 3.63 and 3.08 p.p.m., quite comparable with morpholine. None of these spectra is temperature sensitive, except for the alcoholic group which behaves normally.

The methylene regions of the thermochromic Ia and Ib are complex, with an embarrassment of weak and unresolved lines. Some of these peaks are temperature sensitive and some are not. This can best be seen by reference to the figures and to Table III. Dilution by adding an equal volume of solvent had no effect on the spectrum in any way except to decrease intensity. The sketched spectra (Figure 3) represent the average of a number of runs, but the possibility of weak peaks being lost in the noise should be kept in mind. The most obvious fact is that the symmetry expected of an $A_2B_2$ spectrum is not apparent.

## Discussion

A number of spectra of $>N-CH_2-CH_2-Y$ have been studied.[7,8] In general, these spectra are symmetrical "triplets." More or less fine structure is usually apparent, and the spectrum proves on closer examination to be a standard $A_2B_2$ case. In other cases (R = phenyl or quinonyl with Y = Cl or Br) the two methyl-

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[6] L. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy," Pergamon Press Inc., New York, N. Y., 1959, pp. 91, 108.

[7] P. L. Levins and Z. B. Papanastassion, *J. Am. Chem. Soc.*, **87**, 826 (1965).

[8] W. B. Smith and B. A. Shoulders, *J. Phys. Chem.*, **69**, 579 (1965).

TABLE III

N.M.R. SPECTRUM OF THE METHYLENE REGION OF Ia

| Peaks, c.p.s. (relative peak heights)[a] 37° | 80° |
|---|---|
| 191 (25) | 191 (43) |
| 195 (49) | 195 (57) |
| 199 (98) | 198.5 (100) |
| 203 (100) | 203.5 (87) |
| 211 (88) | 211.5 (96) |
| | 214 (101) |
| 220 (52) | 221 (52) |
| 224 (30) | 225 (34) |
| | 232 (76) |
| 233.5 (73) | |
| 237 (78) | 235.5 (57) |
| | 239 (60) |
| 243 (40) | 243 (26) |
| 246 (20) | |
| | 248.5 (29) |

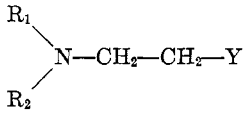
[a] The tallest peak in each spectrum is arbitrarily given the value of 100.

ene multiplets appear much simpler. Ic has a single methylene peak at 231 c.p.s.

The apparent complexity of the spectrum depends on the separation between the methylene multiplets; this is a function of the substituents on the nitrogen and the nature of the Y group. It is apparent from Table III that changing substituents on the nitrogen has its greatest effect on the adjacent methylene, with a lesser effect on the Y methylene, and that this difference measures the change in separation of the centers of the two methylene multiplets. Similarly, changing the Y substituent has about three times as great an effect on the position of the adjacent methylene as it does on the N-methylene (Table IV).

TABLE IV

N.M.R. SPECTRA OF



| $R_1$ | $R_2$ | Y | (N-$CH_2$-) | (-$CH_2$-Y) | Δ, c.p.s. |
|---|---|---|---|---|---|
| H | -$CH_2$-$CH_2$-(O) | -O- | 2.87 (t) | 3.67 (t) | 48 |
| $CH_3$ | -$CH_2$-$CH_2$-(O) | -O- | 2.32 | 3.62 | 78 |
| Quinone | -$CH_2$-$CH_2$-(O) | -O- | 2.97 | 3.72 | 45 |
| $CH_3$ | $CH_3$ | OH | 2.45 (t) | 3.60 (t) | 69 |
| H | H | OH | 2.73 (m) | 3.65 (m) | 55 |
| $C_2H_5$ | Phenyl | OH | 3.40 (m)[a] | 3.72 (m)[a] | 19[a] |
| | | | 3.4[b] | 3.6[b] | 12[b] |
| Quinone | -$CH_2$-$CH_2$-OH | OH | 3.4 (m) | 3.9 (m) | 30 |
| Quinone | $CH_3$ | OH | 3.5 | 3.8 | 18 |
| H | H | OH | 2.73 | 3.65 | 55 |
| H[c] | H | Cl | 2.92 | 3.65 | 40 |
| H[c] | H | F | 2.91 | 4.60 | 101.4 |
| Aziridium[c] | | Cl | 2.41 | 3.55 | 56.4 |
| Aziridium[c] | | F | 2.54 | 4.63 | 131.4 |
| H[c] | Phenyl | Br | | 3.50 (s) | 0 |
| $CH_3$ | Quinone | Cl | | 3.81 (q) | 0 |

[a] In $CDCl_3$. [b] In DMSO. [c] Reference 7.

The solvent also has an effect on the degree of separation as well as the position and appearance of the methylene multiplets. The sensitivity of the methylene separation to the nature of the Y group might provide a sensitive method for determining relative electron release abilities of Y groups by keeping all other factors constant.

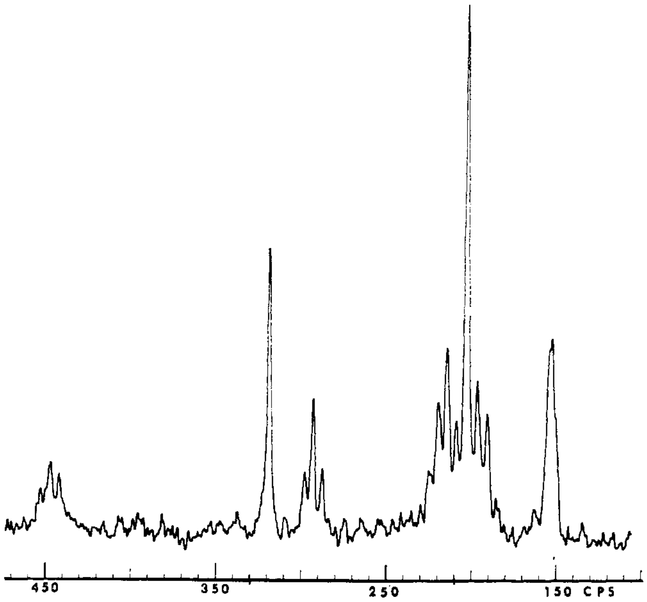


Figure 2.—N.m.r. spectrum of IIa in DMSO-$d_6$. The peak at 150 and the tall peak near 200 c.p.s. are due to DMSO-$d_6$ and DMSO·$H_2O$, respectively.

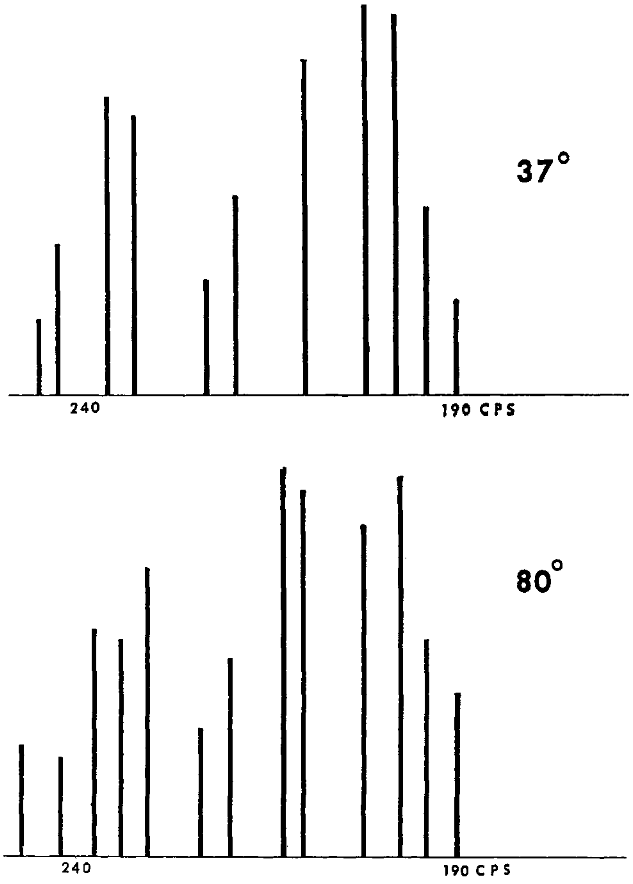


Figure 3.—Methylene region of the n.m.r. spectrum of Ia.

The presence of a second aliphatic group on the nitrogen, or a hydroxyl elsewhere on the molecule, may complicate the methylene region.

The fact that the compound R = H lies intermediate between the thermochromic and nonthermochromic aminoquinones in properties may be owing to competition offered by the hydrogen bonding of the amine hydrogen.

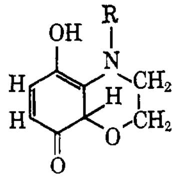
It is not possible from n.m.r. spectra alone to decide whether a heterocyclic ring is formed. Morpholine, 2-aminoethanol, and 4-morpholinoethanol all have widely separated methylene "triplets." However, substitution of an aromatic group on the nitrogen results in bringing these triplets much closer together. The methylene portion of the spectrum of the nonthermochromic 2,5-di(β-hydroxyethyl)amino-1,4-quinone is very like that of N-ethyl-N-phenyl-aminoethanol. The actual spectrum of Ia is almost precisely the same as an overlay of the spectra of the phenylethanolamine and ethanolamine. In neither of these is a heterocyclic ring possible, but they do differ in that one has an aromatic ring on the nitrogen and the other one does not.

That the quinone ring itself is involved in a different way in the thermochromic compounds is shown by the ABX spectrum of the quinone ring protons; that this factor is not part of the thermochromic mechanism is shown by the invariance of this part of the spectrum with increasing temperature.

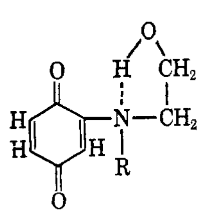
This suggests that the spectrum of Ia is that of two forms of the molecule which differ principally in the degree of aromaticity of the quinone moiety. The temperature-dependent behavior of the methylene portion of the spectrum may be accounted for by a change in the net charge on the nitrogen atom.

Other first possibilities involving the aminoethanol portion would include the formation of an imine, which is ruled out by the fact that the nitrogen methyl group in both Ib and Ic is a sharp singlet at any temperature.[9,10] Another possibility for ring formation involving the nitrogen atom is the formation of an aziridinium ring. Such a ring gives two triplets between 1 and 2 p.p.m.,[7] in a region otherwise vacant. No trace of such triplets appear in the spectra of the quinones reported here.

The structure of the cold form of the thermochromic quinones must be such that the ring protons give an ABX spectrum and that the β-hydroxyl group not be present as an ordinary ethanolic hydroxyl, but that an active hydrogen appear in the phenolic region. This strongly supports an intramolecular reaction between the ethanolic hydroxyl and the quinone moiety. There are several possibilities: 1,4 addition to the C=C—C=O to give V; 1,2 addition to give III; or even possibly a five-membered hydrogen-bonded ring such as VI.



V

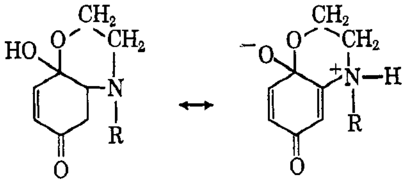


VI

VI is most easily eliminated as a possibility since a hydroxyl hydrogen bonded to a nitrogen gives an n.m.r. peak at about 15 p.p.m., and this would also occur in other β-hydroxyl amines. The possibility of 1,4 addition is harder to role out, but such a structure would probably aromatize very easily to give a stable hydroquinone, with only an AB aromatic n.m.r. spectrum.

1,2 addition to the carbonyl gives III, which fits the n.m.r. spectrum in having an ABX ring proton spectrum, a phenolic proton, and four methylene hydrogens. The heterocyclic ring is not planar, but has a single proton in the plane of the "quinone" ring, and might reasonably be expected to give a spectrum different from a straightforward $A_2B_2$.

The structure of the hot form cannot be that of the simply substituted aminoquinone, since heating does not restore either the ring proton spectrum of the nonthermochromic quinones or the ethanolic hydroxyl which should appear at 4.77 p.p.m. as a triplet. The hot form could be in equilibrium with III as shown below, which would be consistent with the colored form being more ionic, since depth of color and solubility both increase with polarity of solvent.



## Absorption Spectra

The substituted *p*-benzoquinones have been extensively investigated.[11,12] The ultraviolet spectra show a characteristic dependence of the position and extinction of the maxima on the nature, number, and position of the substituents. The relationships referred to are best seen by reference to Table V. Methyl-substituted quinones are characterized by three absorption peaks; in those with an oxygen substituent the second and third peaks are displaced to longer wave lengths, and the third peak is covered by the second.

TABLE V

ULTRAVIOLET–VISIBLE SPECTRA OF SUBSTITUTED QUINONES

| Compound (solvent) | $\lambda_{max}$, mμ (log ε) | | |
|---|---|---|---|
| Methyl[a] (ethanol) | 246 (4.14) | 314 (2.77) | 429 (1.28) |
| (chloroform) | 249 (4.33) | 315 (2.80) | 436 (1.38) |
| Hydroxy[a] (chloroform) | 256 (4.14) | 369 (3.07) | Covered |
| Ic (5-methyl)[b] (methanol) | 220 (4.2) | 280 (4.0) | 480 (3.6) |
| Ib[b] (in phosphate buffer, pH 7.7) | 220 (4.2) | 370 (4.0) | 510 (1.9) |
| Ib[b] (0.1 *M* KOH, 50% methanol) | 220 (4.2) | 310 (4.3)<br>365 (3.4) | 500 (1.2) |
| Ib (water at 25°) | 210 (4.33) | 368 (4.05) | 508 (2.05) |
| Ib (water at 55°) | 210 (4.33) | 368 (4.00) | 508 (2.44) |
| Ib (water, plus trace of acid | 255 (4.2) | 368 (3.3) | Covered |
| Ib (water, plus NaOH) | 210 (4.33) | 275 (3.6)<br>368 (3.3) | Absent |

[a] Reference 11. [b] Estimated from reference 4.

In the nonthermochromic amine-substituted quinones, the second and third peaks are displaced greatly to longer wave lengths. The thermochromic aminoquinones, on the other hand, more closely resemble the normal quinone substituted with an hydroxyl or methoxy group, and without the bathochromic effect of the amino group. This suggests that the hetero-

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(9) R. M. Moriarty, *J. Org. Chem.*, **29**, 2748 (1964).

(10) G. O. Dudek and E. P. Dudek, *J. Am. Chem. Soc.*, **86**, 4283 (1964).

(11) D. M. Grant, R. C. Hirst, and H. S. Gutowsky, *J. Chem. Phys.*, **38**, 470 (1963).

(12) v. W. Flaig, J-C. Salfeld, and v. E. Baume, *Ann.*, **618**, 117 (1958).

cyclic ring is fused to the quinone ring and that the nitrogen is more positive than in the nonthermochromic compounds. Addition of a trace of acid to an aqueous solution of Ib results in a spectrum almost identical with that of a methoxy-substituted quinone; protonation of the nitrogen would have this effect for the structure suggested.

## Summary

Both n.m.r. and ultraviolet–visible spectra suggest that the thermochromic aminoquinones consist of a heterocyclic ring fused to the quinone ring, with the nitrogen bearing a partial positive charge. The thermochromic mechanism consists primarily in a decrease of the positive charge on the nitrogen to restore a more usual charge distribution within the quinone ring.

## Experimental Section

Spectra were run on a Varian A-60 spectrometer. Temperatures were calibrated by substitution of ethylene glycol into the probe. Frequencies were estimated by taking DMSO-$d_5$ as 2.52 p.p.m. (151 c.p.s.), compared with TMS. Spectra were run first at the lowest temperature, then the higher temperatures; on cooling down to the lower temperature the original spectra were reproduced unchanged. Absorption spectra were run on a Cary 14 spectrophotometer.

**Acknowledgment.**—Acknowledgment is gratefully made to K. H. Konig for suggesting the problem and for providing generous gifts of quinones.

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# The Oxidation of Gossypol. II. Formation of Gossypolone with Ferric Chloride

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*Received April 26, 1965*

The oxidation of gossypol (I) with ferric chloride in acetic acid–acetone gave the 1,4-binaphthoquinone II in good yield. Formation of II seemed due to complexation and stabilization of the *o*-hydroxyaldehyde moiety by the ferric chloride and steric blocking of the normal oxidative coupling reaction of phenols.

The 1,4-binaphthoquinone II derived from gossypol (I) has never been prepared although several derivatives were characterized and utilized in the basic work on gossypol structure by Adams and others.[2] Clark[2a] converted gossypol hexaacetate (V) with chromic anhydride to a yellow compound designated by him as tetraacetylgossypolone (Chart I); this experiment was performed prior to knowledge of the structure of gossypol. Clark reported elemental analyses, a molecular weight, and a molecular formula for the product. His molecular formula ($C_{33}H_{30}O_{12}$) does not conform to that for IV ($C_{38}H_{34}O_{14}$), but his elemental analytical data do conform. Later Adams[2b] oxidized gossypol hexamethyl ether with chromic anhydride and obtained tetramethylgossypolone which subsequent work indicated to have the structure VII. Owing to the similar methods of preparation, Adams considered Clark's tetraacetylgossypolone to correspond to IV.[2c]

Mild oxidation of gossypol (I) leads to highly colored products which are probably involved in color fixation in cottonseed oils. We have underway an investigation of the route of oxidative degradation of gossypol under a variety of reaction conditions. In a prior paper[3] we observed the formation of an *o*-binaphthoquinone, 1,1′,6,6′-tetrahydroxy-5,5′-diisopropyl-3,3′-dimethyl-(2,2′-binaphthalene)-7,7′,8,8′-tetraone, from the action of oxygen on gossypol in alkaline solution. We are continuing an investigation of the later stages in this particular oxidative path. The present report deals with the action of ferric chloride in acetic acid–acetone on gossypol. After removal of iron from the initial product, there was obtained in 50–70% yield a quinone of structure corresponding to II. The structure of II is indicated by the n.m.r. spectrum (Table I), infrared spectrum, formation of a tetraacetate derivative (IV), the n.m.r. spectrum of the tetraacetate, and the formation of dianil derivatives III and VI of the quinone and the tetraacetate. The quinone II is 6,6′,7,7′-tetrahydroxy-5,5′-diisopropyl-3,3′-dimethyl-(2,2′-binaphthalene)-1,1′,4,4′-tetraone-8,8′-dicarboxaldehyde but may be designated by the common name "gossypolone" used earlier[2] for derivatives of this substance.

The sample of IV prepared from II was identical with a product made by oxidation of gossypol hexaacetate by the method of Clark.[2a] Both samples of IV melted higher than reported[2a] as did the anil derivatives VI.

Infrared spectra support the structural postulates given above. The carbonyl stretch for gossypol (I) appears at 6.18 $\mu$.[4] Gossypolone (II) shows a band in the carbonyl stretch region which is slightly resolved into two bands appearing at 6.05 and 6.10 $\mu$. These represent the quinone carbonyls and the aldehyde carbonyl, the latter appearing at a somewhat long wave length position owing to the conjugation present. In gossypolone tetraacetate (IV) the aldehyde carbonyl stretch has moved down to 5.85 $\mu$, a normal direction and magnitude of shift for conversion of the hydroxyl group adjacent to carboxaldehyde to an acetoxyl. In addition, the formation of the anil VI caused loss of the 5.85-$\mu$ aldehyde carbonyl stretch.

Attempted methylation of II to produce VII was not successful with several different reaction conditions and reagents.

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(1) To whom communications concerning this paper should be sent.

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