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Chemical Development of Latent Fingerprints: Computational Design of Ninhydrin Analogues

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ABSTRACT: The design of chemical compounds for development of latent fingerprints is explored computationally. Our main findings are: (a) We show why past attempts to improve the widely used ninhydrin gave relatively small improvements (referring to color only). The optical transition is connected with a "transition core" and therefore is influenced little by substitution on the aromatic rings. (b) We propose new analogues of ninhydrin with a significant potential such as thiono derivatives.

KEYWORDS: forensic science, ninhydrin, ninhydrin analogues, Ruhemann's purple, optical absorption, computational, fingerprint development, fingerprints, latent, chemistry

In forensic science ninhydrin (Fig. 1), has become the most important reagent for chemical development of latent fingerprints. The visualization process is based on its reaction with amino acids that are present in sweat to form a purple product; "Ruhemann's purple" (Fig. 2).

In recent years, many ninhydrin analogues have been prepared in an attempt to improve the detectability of latent fingerprints by the reaction. The main desire was to increase the absorption of the product or bring about a color change in its light absorption, or both. Of all the compounds that have been tried, only one, benzo[f]ninhydrin (Fig. 3) gave a distinctively darker color than ninhydrin itself (1–3).

Nevertheless, benzo[f]ninhydrin had several disadvantages as a practical reagent such as cost and solubility and was abandoned as such. Most other ninhydrin analogues developed colors that were quite similar to that of the Ruhemann's purple itself.

This paper presents the results of a series of semi-empirical calculations that explain the small effects of most modifications on the color and the absorption of the product. The paper further outlines chemical variants that may give "Ruhemann's purples" with improved properties.

Method

All the computations were performed using the HyperChem package. Structural models for the ground state were optimized using the AM1 Hamiltonian (4). Structure optimization was carried out until the energy gradient was smaller than or equal to 0.1 kcal/mol. The spectrum was computed with the ZINDO/S model (5). The CI computations for spectrum prediction include three occupied and three unoccupied orbitals.

Results and Discussions

We consider first computations on Ruhemann's purple. The computed optical transitions (absorption) are at 509 and 442 nanometers with oscillator strengths of 0.09 and 0.08 respectively. The experimental λ_{max} is 582 and 404 (6,7). This is an error of about 0.3 electron volt and therefore the exact positions of the lines are qualitative. The above magnitude of the errors for electronic absorption spectrum is typical (see Ref 8,9).

Because of the inherent errors of the calculations, comparison to exact positions of the experimental lines is not useful as a test. Support for the computations can be obtained from the small variations in the line position upon chemical substitution on the rings. Tens of ninhydrins with small spectral shift make an important experimental set that emphasizes the difficulty in improving the common Ruhemann's purple.

Here the computational results are in accord with experiment; little or no spectral shift is observed for many ninhydrin derivatives of the Ruhemann's purple that, for the sake of brevity, are not reported here. Hence, the agreement between theory and experiments for the last observation encouraged us to look for the molecular origin of this phenomenon. The computations provide a guide to the origin of the color and a possible direction for chemical modifications to change it, as explained below. In Fig. 4, we show the highest occupied orbital of a variant of the Ruhemann's Purple (RP) and the lowest empty orbital. The variant is the thiono derivative (see next paragraph). Similar results were found for other related compounds. It is clearly seen that significant changes in the electron density occur at the nitrogen and at the two sulfurs (or oxygens in other compounds), which are closer to the N-H group. This feature was suggested in the past to reflect the anti-aromaticity of the five-member ring (10). However, the computations for the Ruhemann's purple and other compounds discussed below indicate that the transition is focused at the hetero-atoms and is dominant by their corresponding properties (rather than by the properties of the ring). This also suggests that chemical modifications on the rings far from the transition center (that includes the central nitrogen and the oxygens) are unlikely to have a useful effect.

We devote the rest of the article to chemical modifications of the oxygens at the core that (computationally) propose a profound effect in absorption wavelengths and intensities. We consider here two compounds: (a) A substitution of the two carbonyl groups which are closer to the NH bond by C═S groups. In Fig. 4, we

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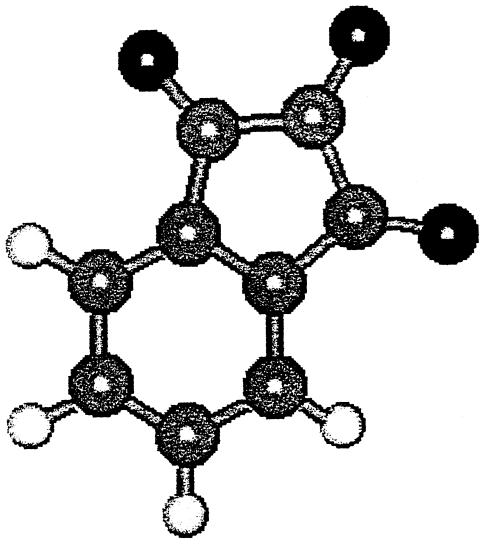

FIG. 1—*A stick and ball model of ninhydrin.*

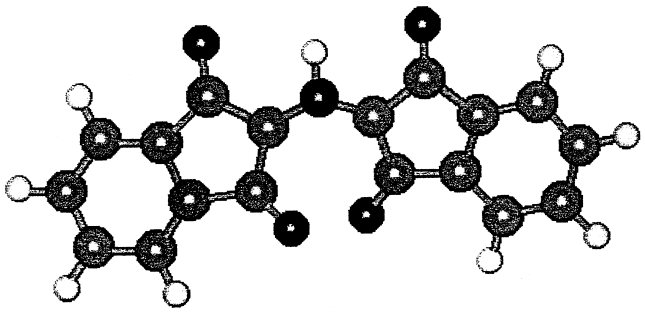

FIG. 2—*A stick and ball model of Ruhemann's purple. Note that the compound is not planar.*

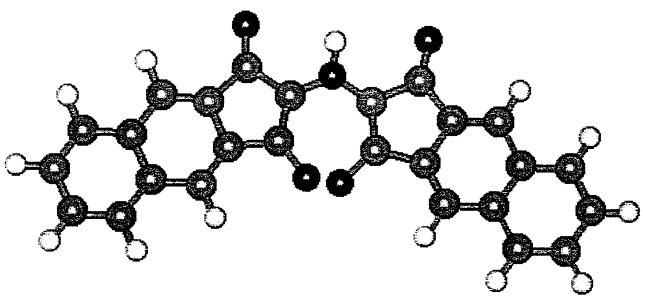

FIG. 3—*A stick and ball model of Ruhemann's purple analogue of benzo[f]ninhydrin.*

TABLE 1—*Electronic structure calculations of ninhydrin analogues. The structures were optimized using the AM1 semi-empirical Hamiltonian and the electronic spectrum was computed with ZINDO/S. See text for more details.*

Compound	Spectra Shift (nanometer)	Oscillator Strength
Ruhemann's purple	0	0.032
Ruhemann's purple (trans) 1-azainden-5,6,7-trione	6	0.032
Ruhemann's purple of 2-azainden-5,6,7,trione	32	0.085
Ruhemann's purple of 2,4-diazainden-5,6,7,trione	39	0.062
Ruhemann's purple of 5-methoxy-ninhydrin	33	1.087
Ruhemann's purple of 4-methoxy-ninhydrin	1	0.061
Ruhemann's purple of 4-hydroxy-ninhydrin	34	1.128
Ruhemann's purple of 5-hydroxy-ninhydrin	30	1.111

show the highest occupied (Fig. 4*a*) and the lowest unoccupied (Fig. 4*b*) orbitals respectively, demonstrating that the transition is local and focuses at the "transition core." The two calculated absorption lines are at 608.46 and 549.30 respectively. While the changes in the color as compared to the Ruhemann's purple are profound, the intensity was not improved. The oscillator strengths were 0.047 and 0.046, respectively and (b) If the two carbonyl oxygens are replaced by methylene (Fig. 5) the color changes are insignificant. However, the oscillator strength increases dramatically by more than an order of magnitude (to 0.833, only one major transition is observed for this compound). This transition is also associated with electron transfer from the nitrogen to the nearby five member rings.

The above examples demonstrate the main point of the present article: the existence of a transition core. Chemical modifications on the transition core have the potential of affecting the optical transition. While the two new compounds proposed above show interesting spectral properties, our calculations did not address the question if the corresponding precursors of the RP analogues react effectively with amino acids. So far, all attempts to prepare the thiono analogues (Fig. 6) of the ninhydrin failed (11). The results for compound (B) are not known.

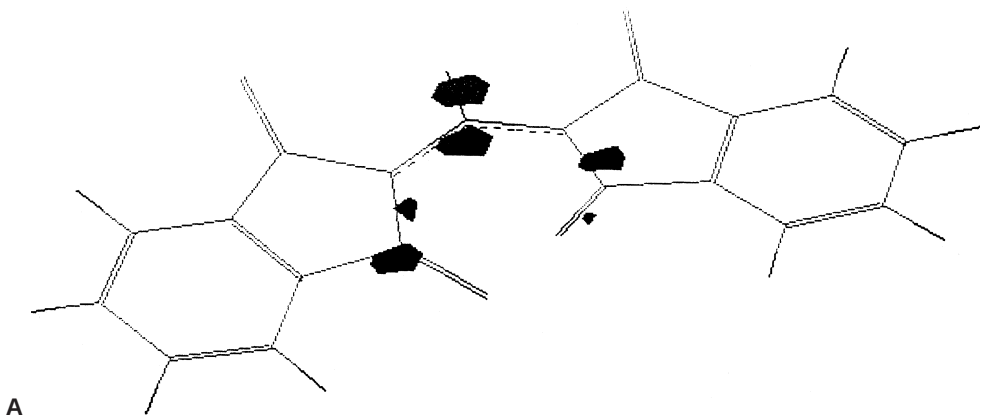

FIG. 4—*The amplitude of the wavefunction at: (A) the highest occupied state and (B) the lowest empty orbital for the C═S analogue of Ruhemann's purple.*

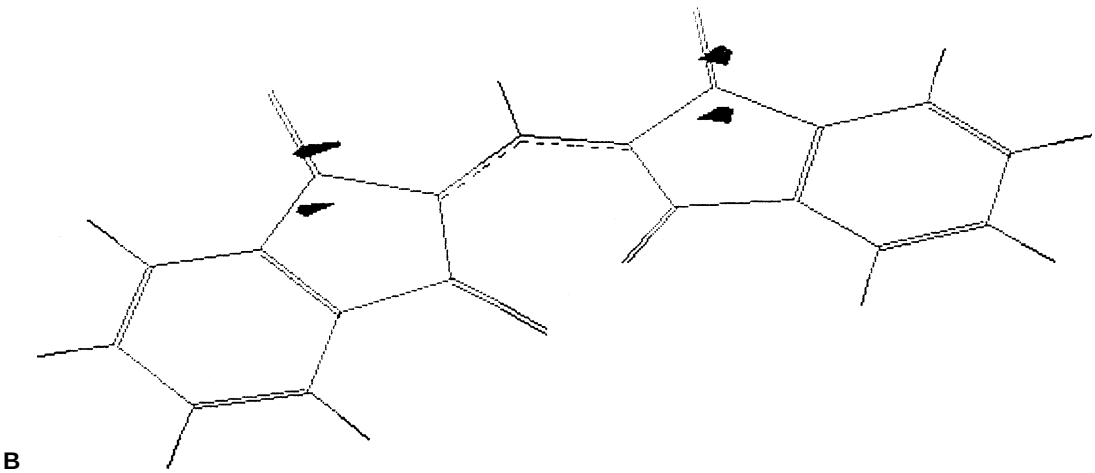

FIG. 4 *(continued)*

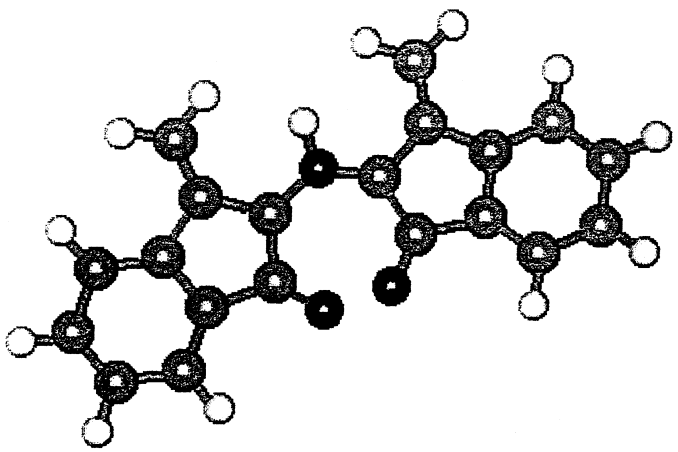

FIG. 5—*The methylene analogue of the Ruhemann's Purple (stick and ball model).*

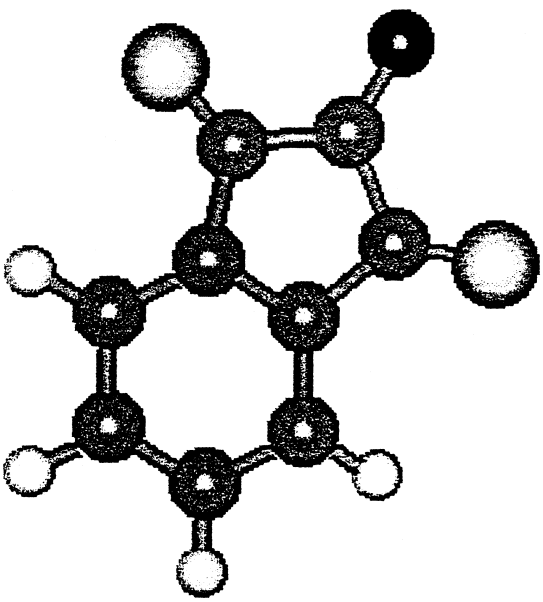

FIG. 6 *(continued)*

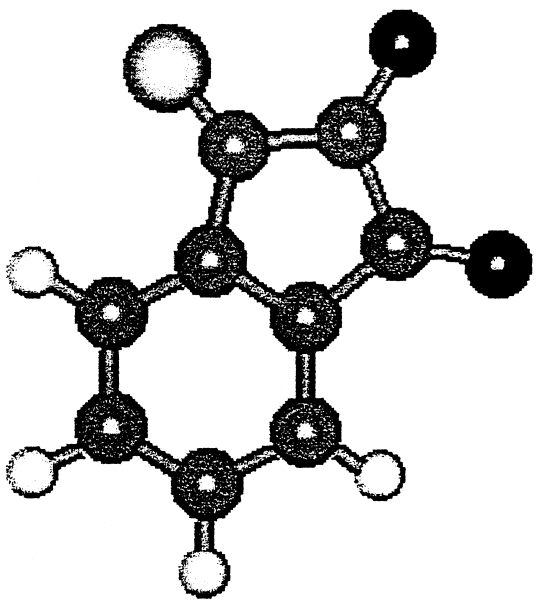

FIG. 6—*The structure of the two sulfur derivatives of ninhydrin (3-thiono-ninhydrin and 1,3 dithiono-ninhydrin).*

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