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[CONTRIBUTION FROM THE CHEMISTRY DIVISION, ARGONNE NATIONAL LABORATORY]

The Alkali Salts of 2,2-Diphenyl-1-picrylhydrazine[1]

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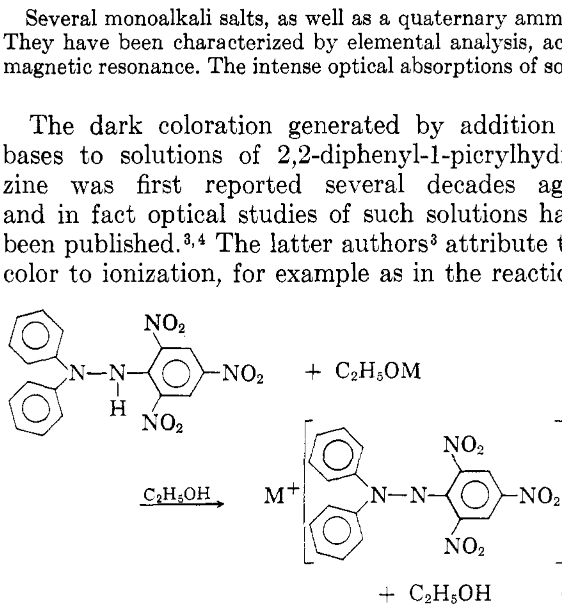
Several monoalkali salts, as well as a quaternary ammonium salt, of 2,2-diphenyl-1-picrylhydrazine have been prepared. They have been characterized by elemental analysis, acid-base titrimetric analysis, and by use of proton high resolution magnetic resonance. The intense optical absorptions of solutions of these salts have been measured.

The dark coloration generated by addition of bases to solutions of 2,2-diphenyl-1-picrylhydrazine was first reported several decades ago,[2] and in fact optical studies of such solutions have been published.[3,4] The latter authors[3] attribute the color to ionization, for example as in the reaction:



(1)

where M is an alkali metal atom. It appears, however, that no further studies of the chemical changes involved have been made. We wish to report such studies, which have led to the synthesis (*via* reaction 1) and characterization of various salts of diphenylpicrylhydrazine including those of lithium, sodium, potassium, rubidium, and also of a quaternary ammonium ion.

The elemental analyses listed in the Experimental section show that the product is essentially the one given by Equation 1. The product is independent of the alcohol used. The black crystalline salts are sensitive to moisture, hydrolyzing to regenerate the diphenylpicrylhydrazine and the corresponding alkali hydroxide, but exhibit no particular tendency to explode. The product is diamagnetic as indicated by the absence of electron paramagnetic resonance (EPR) absorption in the powder or in solution. However, solutions of the salts in acetone shaken with lead dioxide give the typical purple color and EPR hyperfine structure of 2,2-diphenyl-1-picryl hydrazyl (DPPH).

We found it possible to make quantitative molecular weight determinations by carrying out titrations of both the acidic diphenylpicrylhydrazine and its basic salts. With the hydrazine, we followed the procedure given by Fritz *et al.*[5] for titration of nitroaromatic amines, using triethyl-*n*-butylammonium hydroxide as the titrant in a reaction completely analogous to reaction 1; the quaternary ammonium salt produced was isolated and characterized (see Experimental section). Alternatively, titrations with alkali alkoxide solutions were feasible. Similarly, quantitative titrations of the salts of diphenylpicrylhydrazine were carried out by potentiometric titrations with trichloroacetic acid. The molecular weights of the alkali salts thus obtained are reported in the Experimental section; the titrations were accurate to 1–2%. The end product of the titrations of the salts was diphenylpicrylhydrazine, as judged by color and melting temperature (176°).

In general, the salts are soluble in polar organic solvents (acetone, ethanol) and insoluble in the nonpolar ones (benzene, ether). To arrive at some feeling for the relative polarity of the alkali salts, estimates were made of their solubility in 1,4-dioxane (lithium and sodium: 10^{-2} mole $1.^{-1}$ potassium and rubidium: 10^{-4} mole $1.^{-1}$). For comparison, the solubility of diphenylpicrylhydrazine itself was measured and was found to be 0.6 mole $1.^{-1}$.

High resolution NMR results of the salts in acetone, using tetramethylsilane as internal standard,[6] gave additional information. Two proton peaks are observed, with areas in the ratio of 5:1. The larger, occurring at $\tau = 2.90$, arises from the protons on the two phenyl rings, and is little shifted

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission

[2] S. Goldschmidt and K. Renn, *Ber.*, **55**, 628 (1922).

[3] R. H. Poirier, E. J. Kahler, and F. Benington, *J. Org. Chem.*, **17**, 1437 (1952).

[4] A. T. Balaban, P. T. Frangopol, M. Mărculescu, and J. Bally, *Tetrahedron*, **13**, 258 (1961).

[5] J. S. Fritz, A. J. Moye, and M. J. Richard, *Anal. Chem.*, **29**, 1685 (1957).

[6] G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

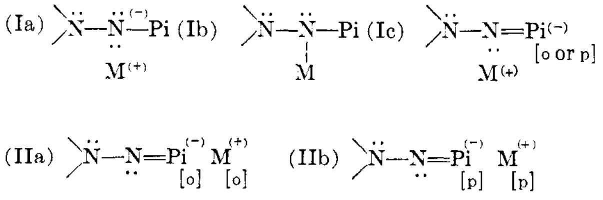
TABLE I

OPTICAL PROPERTIES OF THE ALKALI SALTS

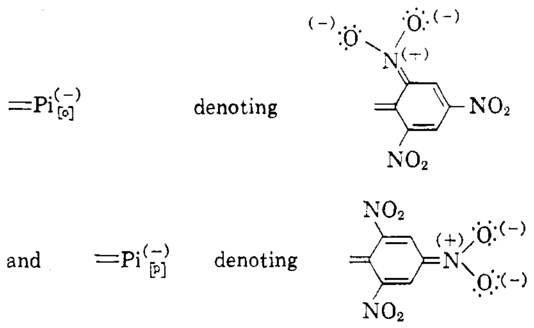
	H	Li	Na	K	Rb	$N(C_2H_5)_3(C_4H_9)$
$\lambda(m\mu)$	320 ± 1	324 ± 1	324 ± 1	324 ± 1	323 ± 1	324 ± 1
$\epsilon(l.\ mole^{-1}\ cm.^{-1})$	1.36×10^4	1.07×10^4	1.19×10^4	1.23×10^4	—	—
$\lambda(m\mu)$	—	424 ± 1	424 ± 1	424 ± 1	421 ± 1	425 ± 1
$\epsilon(l.\ mole^{-1}\ cm.^{-1})$	—	1.14×10^4	1.21×10^4	1.21×10^4	—	—
$\lambda(m\mu)$	$\sim$250	$\sim$250	$\sim$250	$\sim$250	$\sim$250	$\sim$250
$\lambda(m\mu)$	—	$\sim$503	$\sim$503	$\sim$503	$\sim$500	$\sim$500

from the phenyl peak visible with diphenylpicrylhydrazine itself ($\tau = 2.72$).[7] The smallness of this shift indicates that the phenyl rings are little affected by the formation of the negative ion in the salt. The other peak, occurring at $\tau = 1.80$, is caused by the two protons of the picryl ring and is shifted to high-field in comparison with the corresponding protons of the hydrazine itself ($\tau = 1.09$); this shift is consistent with the expected effects of negative charge on the picryl ring. No other proton peaks (except for the alkyl peaks of the NR_4 salt) were found. It thus appears that it is indeed the hydrazine proton (occurring at $\tau = -0.70$ in diphenylpicrylhydrazine), and not a picryl proton, which has been removed. The various salts gave virtually identical NMR spectra.

Optical studies of the alkali salts in ethanol (Table I) give corroboration of the results previously reported.[3,4] The primary peak giving rise to the intense color occurs at 424 mμ with all four alkali ions and also with the quaternary ammonium salt. The lack of dependence of this absorption peak frequency on the nature of the cation implies that the optical transition occurs between states which differ primarily in the electron density distribution of the anionic part of the molecule. The position of the alkali atom within the molecule remains open to question, since it has not yet been established experimentally; an x-ray structural investigation is under way. One can visualize structures of several types



where Pi is the ordinary covalent form of the picryl group, while



are quinoid structures of this group; $M^{(+)}_{[o]}$ and $M^{(+)}_{[p]}$ are the cations bonded to oxygens of the nitro groups *ortho* and *para*, respectively, to the hydrazine link. The presence of the strong optical absorption at 424 mμ in the salts (independent of the cation) and the absence of this peak in the parent hydrazine suggests that the quinoid structures become dominant in the salts. From steric considerations, especially since the large triethyl-*n*-butylammonium ion is able to form a salt analogous to those with alkali alkoxide, it seems more likely that either of structures II occurs in preference to the structures I. The formation of the NR_4^+ salt also indicates that the salts must be highly ionic, since this cation is unlikely to form covalent bonds. The ionic nature of the molecules could allow the M^+ group to be rather nonspecific in its location relative to the rest of the molecule.

Our EPR studies (at 9500 Mc./sec.) of tetrahydrofuran solutions containing both DPPH (0.001 *M*) and the monosodium (or NR_4^+) hydrazine salt at various concentrations (0 to $\sim$0.5 *M*) showed that the salt did not affect the spectrum even when present in high concentration, *i.e.*, no electron transfer between DPPH and M^+-$DPPH^-$ was observable (for example, compare the case of naphthalene and its -1 ion).[8]

It is worth mentioning that the reaction with alkali ethoxide, as described above, has also been studied with the mono- and di*para*-phenyl nitrated derivatives of diphenylpicrylhydrazine (the former of which was until recently thought to be hydroxyhydrazine, see refs. 3 and 7). Preparation of the

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[7] J. A. Weil, K. V. Sane, and J. M. Kinkade, *J. Phys. Chem.*, **65**, 710 (1961).

[8] R. L. Ward and S. I. Weissman, *J. Am. Chem. Soc.*, **76**, 3612 (1954).

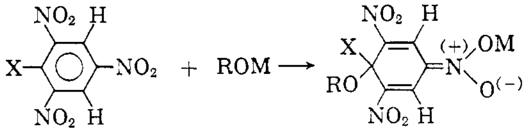
TABLE II

PHYSICAL PROPERTIES OF THE HYDRAZINATES

Formula		M.P.	Mol. Wt.	C, %	N, %	H, %	Alkali, %
$C_{18}N_5H_{12}LiO_6$	Calcd.	—	401.27	53.88	17.45	3.02	1.73
	Found	233°	408.0	54.72	16.85	3.09	1.55
$C_{18}N_5H_{12}NaO_6$	Calcd.	—	417.33	51.81	16.78	2.90	5.51
	Found	248°	419.0	51.91	16.58	3.25	5.25
$C_{18}N_5H_{12}KO_6$	Calcd.	—	433.44	49.88	16.16	2.79	9.02
	Found	259°	437.5	50.27	16.42	2.92	8.71
$C_{18}N_5H_{12}RbO_6$	Calcd.	—	479.81	45.05	14.60	2.52	17.83
	Found	257°	489.0	45.55	14.69	2.79	18.92
$C_{28}N_6H_{36}O_6$	Calcd.	—	552.62	60.85	15.21	6.57	—
	Found	112.5°	548.3	61.03	15.30	6.71	—
$C_{18}N_7H_{10}KO_{12}$	Calcd.	—	523.42	41.30	18.73	1.93	7.47
	Found	270°	527.0	41.30	18.68	2.07	7.17

monopotassium salt of the dinitro derivative is described below. The optical spectra of the dinitrohydrazine show peaks at ~353 ± 1, 450 ± 1, and ~250 mμ, while its potassium salt absorbs at ~348 (weak), 459 ± 1, and ~242 mμ.

Alkali salts of several picryl compounds have been known for years; Meisenheimer,[9] Busch and Kögel,[10] as well as Green and Rowe,[11] have discussed numerous such compounds. It has been suggested[10] that alkali ethoxides can *add* to the picryl ring according to the reaction



. (2)

Addition of up to three alkali atoms has indeed been observed by us in our studies of diphenylpicrylhydrazine. When excess of the alkali ethoxide is added, red powders of low stability are obtained. These will not be discussed further in this paper.

EXPERIMENTAL

The potentiometric titrations were made with a Beckman Model G *p*H meter using a glass electrode (General Purpose) and a calomel electrode (Fiber Type). The diphenylpicrylhydrazine was titrated in pyridine, whereas ethanol containing a little acetone or ethyl acetate was used for the salts. The triethyl-*n*-butylammonium hydroxide was prepared according to the method of Fritz *et al.*,[5] and additional information from Young *et al.*,[12] and was used in benzene solution (*ca.* 0.1 *M*) after standardization with benzoic acid in ethanol. The trichloroacetic acid was also used in benzene (*ca.* 0.1 *M*), and was standardized with the quaternary ammonium hydroxide in ethanol. The alkali ethoxide (or methoxide) was standardized with benzoic acid in ethanol, the typical concentration of ethoxide being 0.2 *M*.

The optical studies were performed with a Cary 14 spectrometer. The NMR measurements were carried out at 60 Mc./sec., using a Varian A-60 instrument calibrated with 40.000 c.p.s. sidebands.

The preparation of the alkali (2,2-diphenyl-1-picryl)hydrazinates. A solution of 2,2-diphenyl-1-picrylhydrazine was prepared in a minimum of dry benzene. An equal number of moles of an alkali metal in absolute ethanol (or methanol) was added with swirling at room temperature.[13] It proved convenient to measure the ethoxide molarity by titration, using the potentiometric method described in the text. On mixing the ethoxide and the hydrazine, the color changed immediately from red-orange to dark brown. The solvent was evaporated by suction. The resulting crystals were recrystallized from a (dried) mixture of benzene or ether and either acetone or ethyl acetate, depending on the specific salt prepared. (The lithium salt was recrystallized from ether only.) It was found that the black shiny crystals contained one mole of acetone or ethyl acetate. To remove this solvation, it was found feasible to heat the crystals at ~100° for 1 hr. A known amount of each salt thus obtained was titrated in ethanol–acetone mixture with triethyl-*n*-butylammonium hydroxide, to measure its molecular weight. The experimental results are summarized in Table II. The melting temperature of the salts varied (*ca.* 5°) with melting conditions.

Potassium (2,2-diparanitrophenyl-1-picryl) hydrazinate. This compound was prepared in a way similar to that for the 2,2-diphenyl-1-picryl hydrazinates, with the following differences: (a) The initial solution was prepared in benzene–ethyl acetate; (b) The brown precipitate was not recrystallized and was titrated in ethyl acetate–ethanol.

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[9] J. Meisenheimer, *Annalen*, **323**, 205 (1902).

[10] M. Busch and W. Kögel, *Ber.*, II, **43**, 1549 (1910).

[11] A. G. Green and F. M. Rowe, *J. Chem. Soc.*, **103** 508 (1913).

[12] W. G. Young, I. D. Webb, and H. L. Goering, *J. Am. Chem. Soc.*, **73**, 1076 (1951).

[13] Addition of exactly equimolar amounts prevented formation of polyalkali salts of the hydrazine.